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EFFECTS OF BORON BEARING ADDITIVES ON HIGH TEMPERATURE PROPERTIES OF DOLOMA-BASED CARBON BONDED REFRACTORIES

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Ce mémoire intitulé :

EFFECTS OF BORON BEARING ADDITIVES ON HIGH TEMPERATURE PROPERTIES OF DOLOMA-BASED CARBON BONDED REFRACTORIES

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RÉSUMÉ

Le but de ce travail a été de déterminer expérimentalement les effets de quatre additifs à base de bore sur les propriétés à température élevées — la résistance à l'oxydation à l'air libre, la résistance à la corrosion vis à vis de trois scories d'aciérage à 1600°C (d'un four à arc électrique, d'une poche d'affinage et d'un convertisseur à oxygène) et le module de rupture à chaud, jusqu'à 1400°C sous atmosphère réductrice – de briques de dolomie et de magnésie-dolomie, à liaison résine, contenant 10% de paillettes de graphite naturel.

Au total, 48 expériences ont été effectuées, en utilisant de l'hexaborure de calcium, CaB_6, du diborure de zirconium, ZrB_2, un produit commercial, Bc, contenant du triborate de magnésium, $(MgO)_3B_2O_3$, et de la colemanite naturelle, chacun avec ou sans mélange de, soit de poudre d'alliage d'aluminium-magnésium, soit de poudre d'aluminium.

(1). Les quatre additifs à base de bore ont un effet marqué sur l'amélioration de la résistance à l'oxydation tant des dolomie-carbone que des magnésie-dolomie-carbone, supérieur à celuie des additifs métalliques (poudres d'Al ou d'Al-Mg). Par ordre de mérite, du meilleur au moins bon, le classement des antioxydants est le suivant : CaB_6 > Bc > ZrB_2 > colemanite. La quantité optimale à utiliser pour la résistance à l'oxydation se situe au niveau de 3 à 4 %. L'utilisation d'antioxydants mixtes (additifs borurés en présence d'additifs métalliques) est très efficace, grâce aux effets synergiques qui se développent lorsque les deux types sont présents.

(2). L'effet remarquable des additifs borurés sur le comportement à l'oxydation est attribué à la formation d'un liquide protecteur, à base de borate, et où le borate de calcium, $Ca_3B_2O_6$, est prédominant. Cette phase protectrice ralentit l'oxydation des carbones des échantillons. L'effet est d'autant plus net que la température d'oxydation est plus élevée, en proportion à la quantité de borate liquide qui croît avec la température.

(3). Selon les résultats des essais de résistance à la corrosion, effectués au four rotatif, les additifs borurés ont un effet négatif, tant sur les dolomie-carbone que sur les magnésie-dolomie-carbone. Ceci serait dû à la trop grande quantité de borate liquide, formé à 1600°C, qui favorise la dissolution des grains d'oxydes. Toutefois, l'utilisation d'antioxydants mixtes, additifs borurés- additifs métalliques, est favorable à l'amélioration de la résistance à la corrosion par rapport aux réfractaires graphités de même nature sans aucune addition anti-oxydante. Encore une fois, l'effet de synergie joue en faveur des mélanges mixtes.

Dans tous les cas de corrosion, la zone pénétrée dans chaque échantillon est très faible (inférieure à un millimètre d'épaisseur), parce que la phase liquide de borate s'interpose entre les grains d'oxydes et le graphite d'une part, et la scorie de l'autre.

(4). Les quatre additifs borurés ont un effet très peu marqué sur la valeur du module de rupture à chaud, mesuré sous atmosphère réductrice, parce que sous ces conditions les borures ne fondent ni ne réagissent rapidement. Toutefois, les additions mixtes (métaux et non-métaux) sont, elles, très favorables. Pour le rapport borure: aluminium de 1 à 3, en % poids, la valeur du module de rupture à 1400°C double par rapport au réfractaire équivalent sans aucun additif. Ce gain est surtout dû à la

contribution de l'aluminium, qui, sous atmosphère réductrice, se transforme en Al_4C_3, provoquant une augmentation notable de la résistance mécanique.

(5). En se basant sur les résultats précédants, de façon à optimiser les propriétés à haute température des dolomie-carbone et des magnésie-dolomie-carbone (tant oxydation que corrosion et résistance mécanique sous atmosphère réductrice), il est recommandé d'utiliser des antioxydants mixtes : additifs borurés - alliages métalliques selon un ratio ajusté aux conditions de mise en service prévues. Un travail complémentaire de développement pour optimiser ce ratio mériterait d'être effectué, à court terme.

ABSTRACTS

The aim of this work was to determine experimentally the effects of four boron bearing additives (CaB_6, Bc, ZrB_2 and colemanite) on high temperature properties — the oxidation resistance in air; the corrosion resistance to various steelmaking slags (EAF slag, secondary refining slag and BOF slag) and on the hot modulus of rupture, up to 1400°C under reducing conditions, of resin bonded doloma and resin bonded magdoloma bricks, containing 10 % of natural flak graphite.

In total, 48 experiments have been performed, using calcium boride (CaB_6), zirconium diboride (ZrB_2), a commercial product — Bc, containing magnesium and boron oxides, and a hydrous colemanite, mixed with either aluminum-magnesium alloy or aluminium fine powder.

(1). Boron bearing additives have marked effects on improvement of oxidation resistance of doloma-carbon and magdoloma-carbon materials, much better than that of metallic additive (Al powder or Mg-Al alloy). The order of merit as antioxidants is CaB_6 > Bc > ZrB_2 > colemanite > alloy. The optimum addition amount of boron bearing additives for oxidation resistance is 3 ~ 4 %. Mixed additives (boron bearing additives and Mg-Al alloy or Al powder) are also very effective as antioxidants due to synergetic effects of the two types of additives.

(2). The remarkable effect of boron bearing additives on oxidation behavior is found to be attributed to the formation of borate melt protective layer, during oxidation, the borate being predominantly $Ca_3B_2O_6$. This protective layer would impede or retard

carbon oxidation in the materials. With increase of temperature, oxidation resistance is observed to increase because the borate melt is formed more quickly and more readily at high temperature (1400°C ~ 1600°C)

(3). Boron bearing additives are found, using a dynamic rotary test to be negative to slag corrosion of doloma-carbon and magdoloma-carbon materials. This may be due to the effect of borate melt which would be beneficial at first stage of slag corrosion (carbon oxidation), but detrimental at second stage of slag corrosion (chemical corrosion). However, mixed addition of boron bearing additives and metal powder results in pronounced improvement in slag resistance. This is also because of the synergetic effects of the two types of additives.

The reaction zone of all specimens with boron bearing additives after slag tests is very thin (< 1mm) at all temperatures tested which is due to the presence of borate melt acting as a barrier to prevent or slow done slag penetration.

(4). Boron bearing additives have insignificant effect on hot strength tested under reducing atmosphere, because boride added is found to have no changes in composition or structure; no noticeable decomposition of boride has been observed. However, mixed addition with appropriate ratio of boride and metal additive, does improve strength properties, at elevated temperatures under reducing conditions. When boride / Al ratio is 1 : 3, HMOR at 1400°C is almost doubled as compared with specimen without additive. This again is due to synergetic effects of the two types of additives. Contribution of Al additive on hot strength is more pronounced because Al_4C_3 formed causes a net strengthening effect.

(5). Based on the above results, for optimization of high temperature properties (oxidation resistance, corrosion resistance and hot strength) of doloma-carbon and magdoloma-carbon materials with emphasis on antioxidation, it may be concluded that mixed additives of boron bearing additives and metal powder with proper ratio according to the service conditions of applications should be adopted. Developmental work should be considered and organized in this direction.

CONDENSÉ EN FRANÇAIS

RÔLE D'ADDITIFS BORURÉS SUR LES PROPRIÉTÉS DES RÉFRACTAIRES DE DOLOMIE À LIAISON CARBONE

1. Le cadre général et le but de l'étude

L'utilisation du graphite dans les briques de dolomie est limitée parce qu'il n'y a pas d'antioxydant adéquat pour protéger le carbone. Sur le plan commercial aujourd'hui la quantité de graphite est limitée à quelques pourcents, la quantité totale de carbone résiduel à 7 %. Cette limite n'existe pas pour les briques de magnésie à liaison carbone. L'antioxidant usuel, bon marché et tout à fait adéquat est l'aluminium. Si l'on cherche à utiliser un tel oxydant dans des briques de dolomie-carbone, on se heurte au problème de la formation d'aluminates de calcium à bas point de fusion.

Le premier défi à relever dans ce travail était donc de prouver qu'un composé boruré seul ou en conjonction avec une poudre métallique, aluminium ou alliage d'aluminium-magnésium, pourrait être adéquat.

Le deuxième objectif a été de comparer le comportement de briques de dolomie à celui de briques de dolomie enrichie de magnésie, à partir d'un agrégat cofritté de dolomie-magnésie, toujours dans le cas de briques à liaison carbone, avec 10 % de graphite et un niveau total de 4 % d'antioxydants.

Ce travail se situe dans le cadre du prolongement de la thèse de doctorat de

Pascal Bombard, intitulé "Évaluation du B_4C comme antioxydant dans les réfractaires basiques à liant carbone", dans laquelle une partie des essais avait porté sur des briques expérimentales de dolomie, thèse soumise en septembre 1994. Dans ce premier travail, il avait été démontré que l'addition de carbure de bore était très significative; compte tenu du coût de cet additif, il a été décidé de reprendre le travail en vérifiant l'effet de plusieurs autres composés borurés: le borure de calcium, CaB_6, le borure de zirconium ZrB_2, un produit commercial à base de borate de magnésium $3MgO{\cdot}B_2O_3$ (M_3B) , et finalement un minerai naturel de bore: la colemanite. Pour minimiser la quantité de bore à ajouter, il fut aussi décidé dès le début des travaux de vérifier des additions mixtes de borures et de poudres métalliques. Cet effet synergétique des deux types d'antioxidants a été maintes fois observé et documenté dans la littérature et dans les travaux des chercheurs du CIREP.

Dès lors le but de ce mémoire a été de déterminer expérimentalement les effets des quatre additifs à base de bore, ci-dessus mentionnés, sur les propriétés, entre 1000 et 1600 °C, à savoir la résistance à l'oxydation à l'air libre, la résistance à la corrosion vis à vis de trois scories d'acierage, et le module de rupture à chaud, jusqu'à 1400 °C sous atmosphère réductrice.

Dans ce condensé, seront décrits les aspects concernant la fabrication des briques expérimentales, les procédures expérimentales et les principaux résultats obtenus, le tout se terminant sur une discussion générale débouchant sur des perspectives de collaboration entre CIREP et l'Institut de Recherche en Réfractaires de Luoyang, en Chine (LIRR).

2. Élaboration des briques de dolomie et de mag-dolomie

2.1 Matières premières

La dolomie utilisée a été fournie par un partenaire industriel du CIREP, possédant un gisement de dolomite. Elle a été livrée, calcinée, en cinq fractions distinctes 3 à 7, 7 à 14, 14 à 30, 30 à 60 et -60 mesh; une fraction de -200 mesh a aussi été tamisée, après broyage, sur place. Les agrégats de magnésie-dolomie ont été reçus directement de l'LIRR avec les mêmes granulamétries: 5 tailles. Les compositions chimiques des 2 agrégats sont reproduites au Tableau 1 suivant.

Tableau 1. Composition et densité des agrégats de dolomie et de magnésie utilisées

Composition (%)	Dolomie	Magdolomie
MgO	41.0	71. 10
CaO	57.0	25.50
Fe_2O_3	1. 0	0. 90
SiO_2	0.6	1. 27
Al_2O_3	0.4	0.76
Densité (g / cm^3)	3.25	> 3.25

Le graphite utilisé était un graphite provenant du Lac des Iles (Québec); ce graphite

naturel en pallettes avait une pureté de 96 % en carbone, la composition chimique des cendres est donnée au Tableau 2 suivant :

Tableau 2 -- Composition chimique des cendres du graphite

SiO_2	Al_2O_3	Fe_2O_3 (total)	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_3	SO_3	P.A.F. 1100°C
37.3	9.69	12.0	8.9	20.9	1.46	2.23	0.38	0.12	0.12	1.67	4.63

Parmi les additifs borurés il convient de préciser ici la composition chimique de la colemanite, obtenue directement d'un fournisseur turc; voir Tableau 3 ci-après.

Tableau 3 -- Composition de la colemanite

Compositions	Minimum (%)	Maximum (%)
B_2O_3	40.00	42.00
CaO	23.50	24.50
Soufre total	0.40	0.60
Fe_2O_3	0.40	0.55
Al_2O_3	2.30	2.60
MgO	1.40	1.70
K_2O	0.03	0.06
Na_2O	0.01	0.02

Pour ce qui est du détail des autres matières premières utilisées il faudra consulter le texte en anglais, Chapitre 3.

2.2 Élaboration des briques expérimentales

La procédure détaillée pour la production des briques se retrouve dans la partie anglaise aux pages 34 à 44. Toutes les briques contenaient 10 % de graphite et 5% de résines phénoliques. La formulation des briques de dolomie et de magdolomie est détaillée dans les Tableaux 4 et 5 et les caractéristiques principales des briques dans le Tableau 6.

Tableau 4. Formulation des 3 séries de briques de dolomie-carbone, montrant les pourcentages poids d'additifs utilisés dans chaque cas

Dénomination	CaB_6	Bc	ZrB_2	Colemanite	Mg-Al alloy
DC*	4	-	-	-	-
DS*	-	4	-	-	-
DZ*	-	-	4	-	-
DB	-	-	-	5	-
DA	-	-	-	-	4
DCA	2	-	-	-	2
DSA	-	2	-	-	2
DZA	-	-	2	-	2
DSA 1:2	-	1	-	-	2
DSA 0.5:2	-	0.5	-	-	2
DSA 1:3	-	1	-	-	3
DSA 0.5:3	-	0.5	-	-	3

Tableau 5. Formulation des briques de mag-dolomie carbone

Dénomination	Additifs
MDC	CaB_6 4 %
MDS	Bc 4 %
MDZ	ZrB_2 4 %
MDA	Alloy 4 %
MDCA 2:2	CaB_6 2 % + alloy 2 %
" 1:2	" 1 % + " 2 %
" 0.5:2	" 0.5% + " 2 %
" 0.5:3	" 0.5% + " 3 %
" 1 : 3	" 1 % + " 3 %

Tableau 6. Principales caractéristiques des briques expérimentales

Dénomination	Porosité (%)		Densité (g/cm^3)		MDR (MPa)
	à vert	carbonisé	à vert	carbonisé	à vert
DO	3.10	12.70	2.78	2.68	14.71
DA	4.06	12.22	2.72	2.67	16.68
DB	6.85	16.63	2.64	2.57	11.74
DZ	4.20	11.90	2.81	2.74	14.54
DS	5.09	11.13	2.71	2.69	12.29
DC	4.66	12.02	2.71	2.67	13.63
DZA	4.05		2.84		17.57
DSA	4.56		2.79		14.57
DCA	4.15		2.80		15.22

3. Procédures expérimentales

Le protocole expérimental suivi pour déterminer les résistances à l'oxydation et à la corrosion, est celui qui a élaboré au CIREP au cours des années; une brève description en est faite dans la version anglaise, aux pages 45 à 48. Un seul point mérite d'être souligné dans ce condensé. Les essais de détermination des modules de

rupture à chaud en atmosphère réductrice ont été conduits dans les laboratoires de l'LIRR, par l'auteur lui-même, qui est retourné en Chine, pour six mois, afin de compléter ce travail.

Au total, 48 expériences ont été effectuées pour les essais d'oxydation, 18 expériences pour les essais de corrosion et 9 expériences pour la détermination des modules de rupture. Une étude microstructurale et une de caractérisation par diffraction-X ont été menées sur les échantillons les plus performants DC, DS, DCA et MDC, MDCA. Les précisions sont fournies dans le corps principal du mémoire.

4. Résultats obtenus

Les principaux résultats sont représentés dans les figures 13, 17, 23 et 29 du texte anglais. La signification de ces résultats a été résumée dans les pages viii à x précédentes. Ce texte ne sera pas repris ici.

5. Discussion et perspectives d'avenir

Le but de ce travail expérimental a été atteint puisque les effets des différents anti-oxidants ont été clairement identifiés.

La partie la plus significative de ce travail c'est qu'il a été mise en évidence qu'il sera possible de produire des briques de dolomie avec au moins 10% de graphite, ce qui offre des perspectives de commercialisation intéressantes, favorisant la compétition dolomie versus magnésie. Les anti-oxidants mixtes composés borurés-

alliages sont performants; il conviendra maintenant d'optimiser les mélanges selon les propriétés ultimes recherchées.

L'autre aspect significatif de ce travail c'est que nous avons constaté que les briques de mag-dolomie-carbone fabriquées à partir d'un agrégat "unique" sont supérieures aux briques de dolomie-carbone.

Dans les perspectives d'avenir que ce mémoire ouvrent, il conviendra de retenir les deux aspects précédents. Il est espéré que la collaboration IRRL et CIREP se poursuivra et incluera des travaux avec cette classe de matériaux. Plusieurs projets de nature plus scientifique, s'attaquant à la compréhension des mécanismes intimes des réactions complexes qui se déroulent dans ces systèmes sont à réaliser.

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CHAPTER 1. INTRODUCTION

Since BOF steelmaking process has been adopted, carbon–containing basic refractories used for the furnace lining have undergone the following evolutions:

--- pitch–bonded brick,

--- pitch–impregnated burned brick,

--- carbon–bonded brick.

Carbon bonded basic refractories (magnesia-carbon, magdoloma-carbon and doloma-carbon brick) have been popularly employed in EAF furnace, secondary refining vessels and slag line of ladle in recent years. Since the late seventies, carbon bonded refractories have been developed very rapidly in production capacity, in product quality and varieties and in areas of applications. They have dominated many important application area in metallurgy and their usage has led to considerable increase in service lifes and reduction in refractories consumption, contributing much to the development of the steel industry. For example: the campaign life of BOF lining has increased from several hundreds heats to several thousands heats after the use of magnesia-carbon brick. In this development, magnesia-carbon brick has taken the lead and much work in research development has been carried out for its improvement in technology, properties and service performance. Relatively speaking, use of doloma-carbon brick (including magdoloma-carbon brick) has been developed at a slower rate and less work has been done; but with the advent of clean steel technology, it has gained increased attention

and is expected to increase in importance in the coming years. In the next fifteen years, at the turn of the century it may be predicted that carbon-bonded basic refractories will continue to flourish with new development in product quality and varieties, improvement in high temperature properties and important in service performance, especially in guaranteeing steel quality. Magnesia-carbon brick will still be in the lead, but, doloma-carbon (including magdoloma-carbon) brick will develop at a faster rate to cope with the requirements of clean steel technology which will be one of most important strategic developments in steel metallurgy in the new century[1-5].

In terms of corrosion resistance to basic steelmaking slag, doloma (magdoloma) is inferior to magnesia, but in the case of carbon-bonded refractories, this disadvantage of doloma should be less significant because carbon is the primary factor determining corrosion resistance. In magnesia-carbon brick, MgO in contact with carbon react together at high temperature (1600°C or so) as follows:

$$MgO_{(s)} + C_{(s)} \rightarrow Mg_{(v)} + CO_{(v)} \qquad [1\text{--}1]$$

$$2Mg_{(v)} + O_2 \rightarrow 2\,MgO \qquad [1\text{--}2]$$

However, in the case of doloma-carbon brick, the presence of free CaO would inhibit this redox reaction of MgO, because CaO is more stable at high temperature than MgO. More importantly, from the metallurgical view point, free CaO in refractories would be beneficial to steel quality; it may reduce the amount of inclusions in steel to some extent. Besides, doloma is generally cheaper than magnesia, therefore, considering overall technical and economic effectiveness, and considering the more widespread adoption of clean steel technology, it may be predicted that the future steel industry, demand for

high performance doloma-carbon and magdoloma-carbon refractories will noticeably increase.

In general, the properties of refractories, most closely correlated to service performance, are high temperature strength properties (hot modulus of rupture, hot crushing strength, modulus of elasticity, fracture toughness, creep resistance), thermal-shock resistance, and corrosion resistance. In the case of carbon bonded materials, oxidation resistance should be considered in addition. The reason for the fast development of carbon bonded basic materials is that they possess very good thermal-shock resistance and slag corrosion resistance; the former is because of their structural flexibility and high thermal-conductivity and the latter is due to the non-wettability of carbon to slag. However, they have two weaknesses — poor oxidation resistance and low hot strength. Therefore, it is very important to find out ways to improve oxidation resistance and hot strength of this materials. Antioxidation should be considered first because when carbon is oxidized, the two important excellent properties, thermal-shock resistance and slag corrosion resistance are lost.

In recent years, considerable research and development work has been conducted on the improvement of oxidation resistance of carbon bonded basic refractories and much progress has been made. For example, the addition of metal powder (Al, Mg-Al alloy) to magnesia-carbon brick has resulted in noticeable increase in oxidation resistance as well as in hot strength. This is now universally adopted in manufacture and technical and economic effectiveness has been attained in practical applications. To seek for more effective antioxidant, boron bearing materials, such as boron carbide, C_4B,

have been investigated for the effect on oxidation resistance of carbon bonded basic refractories; most of the work are related to magnesia-carbon bricks, indicating the effectiveness of B_4C[6,7]. In the last few years, fundamental research on the effects of metallic boride, such as B-Mg material has indicated that mixed addition of boride and metal powder is effective. However, little work has been reported in literature about research and development on the effects of boron bearing antioxidants on doloma-carbon and magdoloma-carbon materials. M. Rigaud and his co-workers have carried out investigations on the effects of B_4C on doloma-carbon materials[8,9]. In view of the good prospects of doloma-carbon and magdoloma-carbon materials, as described above, more work should be focused on the improvement of their oxidation resistance by incorporating more effective antioxidants such as boron bearing materials and its mixed addition with metal powder (Al or Mg-Al alloy). Besides, oxidation resistance, slag corrosion resistance and hot strength should also be studied in parallel, so that optimization of high temperature properties with emphasis on oxidation resistance may be suggested and organized for high performance doloma-carbon product. This is the main purpose of this work.

The aim of this work is to determine effects of boron bearing additives on high temperature properties (oxidation resistance in particular) of carbon bonded MgO-CaO refractories in air and to elucidate the mechanism of the reactions during oxidation and corrosion in contact with slag. As a result, new avenues will be explored to develop high performance doloma-carbon and magdoloma-carbon bricks with improved oxidation resistance without impairing slag corrosion resistance and hot strength properties.

This research program is a cooperative project between Ecole Polytechnique, Montreal, Canada and Luoyang Institute of Refractories Research (LIRR), Luoyang, China, which is a part of an overall scientific cooperation between the two institutions. The experimental work of this program on oxidation tests (box furnace and rotary furnace methods) and slag corrosion tests (rotary test method) was carried out at CIREP, Ecole Polytechnique. Other corrosion tests (crucible test method) and hot modulus of rupture (HMOR) tests were done at Luoyang Institute of Refractories Research. Phase composition and microstructure of specimens before and after tests were examined by XRD and SEM in both institutions

In this thesis, the following points are reported:

1). The background and current situation of studies on improvement of properties of carbon-containing basic refractories (including magnesia-carbon, magdoloma-carbon and doloma-carbon materials) are introduced. The characteristics and applications of CaO–MgO–C refractories are reviewed.

2). The composition and properties of raw materials and additives are given for the experiments, and formulations of specimens tested as well as specimen preparation are described.

3). The testing methods and their characteristics for oxidation resistance, slag corrosion resistance and hot MOR tests are reported.

4). Studies on the effects of boron bearing additives on oxidation resistance of doloma-carbon and magdoloma-carbon refractories are presented. They include various

types of boron bearing additives, in variable amount of boron bearing additives and various proportions in mixtures with Al-Mg alloy.

5). Studies on the effects of boron bearing additives and its mixed addition with Mg-Al alloy on slag corrosion resistance of the doloma(carbon and magdoloma(carbon specimens using three types of slag with different basicity are presented.

6). Studies on the effects of boron bearing additives and its mixed addition with Al powder on hot modulus of rupture (HMOR) of doloma–carbon and magdoloma–carbon specimens under reducing atmosphere are reported.

7). Finally, after the discussion and interpretation of the experimental results, the overall effects of boron bearing additives and its mixed additives with metal powder on high temperature properties of doloma-carbon and magdoloma-carbon materials are evaluated. Their behavior and action mechanisms are discussed. Recommendations for formulations of optimum additives to obtain optimized high temperature properties are given for different practical applications. Suggestions are made for developmental work on doloma-carbon (magdoloma-carbon) refractories with boron bearing additives and on further in-depth study.

CHAPTER 2. PERSPECTIVES ON DOLOMA– AND MAGDOLOMA–CARBON REFRACTORIES

Before the 1980's, pitch–bonded bricks and pitch–impregnated burned bricks constituted the main furnace lining materials for BOF steelmaking. In this refractories, the carbon came from carbonization of pitch or tar was amorphous, and its content in bricks was not high (less than 5 %). The carbon played mainly the role of filling the pores. Campaign lifes of the refractories were in the 400 to 800 heats range. With development of top and bottom combine blowing LD, UHP-EAF and secondary refining vessels, high temperature properties of previous refractories were not satisfactory for modern steelmaking technology. New technology and new equipment in metallurgical industry require a overall balance of optimized refractory properties, including hot strength, thermal shock resistance, slag corrosion resistance and oxidation resistance etc. Generally, improvement of some properties is often accompany with contradiction to other performance, for example: decreasing porosity and increasing bulk density are good for improvement of slag corrosion resistance, but lead to a decrease of thermal shock resistance. This contradiction was solved by means of adding graphite in bricks. Of course, new problems arise as old ones are resolved, hence oxidation of graphite and protection of carbon became a key point for carbon containing refractories. As it is well known, graphite offer non–wettability characteristics to molten slag and good thermal conductivity, but require some protection to oxidation. In this chapter, the properties and

characteristics of the starting materials for carbon containing basic refractories , are reviewed and applications of this refractories are also reported.

2.1 Doloma and Magdoloma (dead-burned clinker)

Mineral dolomite is composed of double carbonate of calcium and magnesium in equal molecular proportions [$CaMg(CO_3)^2$]. The mineral theoretically contains 30.4 % CaO (54.3 % $CaCO_3$), 21.7 % MgO (45.7 % $MgCO_3$) and 47.9 % CO_2 . CaO / MgO ratio is equal approximately to 1.39. The term rich calcium dolomite will be used to describe the mineral with a ratio CaO / MgO greater than 1.39; if MgO content is higher and ratio CaO / MgO is less than 1.39, it is then called magdolomite.

There is a limited number of dolomite deposits in the world which have satisfactory uniformity, purity and calcining behavior, to be processed economically into a high purity raw material suitable for the production of doloma refractories. Dolomite usually contains some impurities which are often associated with accessory minerals. These impurities typically consist of silica, alumina, iron, manganese, sulfur and phosphorous. The term doloma refers to the calcined dolomite. Refractory grade dolomite is usually high purity. The high purity dolomite are generally considered to contain less than 3 % impurities and greater than 97 % CaO + MgO. Most high purities dolomite deposits are difficult to calcine and sinter to high density and usually require special methods to yield an acceptable refractory grade doloma[10,11].

Silica, iron oxide and alumina are the most common impurities in high purity doloma. Since the impurity content is very low, the dolomite is not easily calcined. Temperature in excess of 1850 °C are usually required for calcination of the dolomite in order to achieve satisfactory density and hydration resistance[12].

Fig. 1 is the CaO–MgO system phase diagram[13]. The eutectic temperature of MgO and CaO in this system is 2370 °C, it is much higher than required for most steel making applications, even if the presence of impurities will decrease the temperature at which a liquid phase will occur.

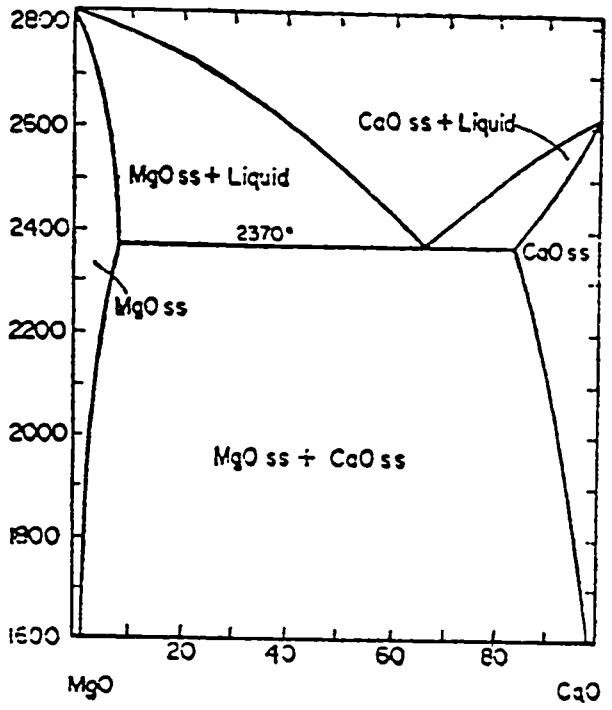


Fig. 1 CaO–MgO system phase diagram

The use of doloma as a refractories was first started in 1878 when doloma was used as linings in open hearths furnace or Thomas converters[14]. In the last twenty years, there has been a significant growth in the use of high purity doloma refractories for steel

applications. This is primarily due to an increase in basic steelmaking process to produce higher quality steel with precise metallurgical control. Doloma refractories are well suited for usage in many of these steel applications due to their high refractoriness and compatibility with basic slag.

Doloma is an excellent refractory since it is thermodynamically stable in contact with slag. CaO is more stable than the other usual refractory oxides, as shown by the free energy of formation values listed in Table 1.

Table1. Free Energy of Formation for Various Refractory Oxides[15]

Reaction	ΔG°, (1600 °C)
$2Ca + O_2 = 2\,CaO$	-205
$4/3\,Al + O_2 = 2/3\,Al_2O_3$	-175
$2Mg + O_2 = 2\,MgO$	-170
$Si + O_2 = SiO_2$	-140
$4/3\,Cr + O_2 = 2/3\,Cr_2O_3$	-110

Therefore, CaO containing material is more suitable for the refining processes where Ca, Si and Al are used as reactive agents.

2.2 Carbon Material

Carbon for refractories come from various carbon composites materials, such as, natural flake graphite, synthetic graphite, metallurgical-tar, coal coke, pitch, pitch-tar, petroleum–tar and so on. Historically, graphite bearing refractories have been known for at least 200 years[16]. Despite its highly refractory nature and its interesting mechanical and thermal properties, graphite can not operate alone in a large number of hostile environments. This , of course, is due to the relative ease with which it is oxidized. The combination of clay and graphite for crucibles was indeed a precursor. The object, whether by design or accident, was to protect the graphite from oxidation and to endow the clay, with thermal properties such as conductivity and thermal shock resistance. Also the graphite raised the refractoriness of the crucibles in which they were used since, although the clay would soften at high temperature, the graphite would maintain a coherence within the body.

The principal combinations which are now in current use, are graphite with either Al_2O_3, MgO, CaO, ZrO_2 and SiC as major constituents with lesser but nonetheless important minor additions to improve oxidation resistance and bonding. The range of combination is diverse with graphite levels between 10 and 40 % by weight.

Natural graphite is a non-metallic mineral. Its occurs in three forms: flake, amorphous and high-crystalline[17]. The flake graphite for refractories applications are classified according to the flake size and carbon content. As mined, graphite exhibits different flake sizes, described as coarse, medium and fine flakes. The flake size can range from micron up to millimeter. The highest purity flake graphite can contains greater than 99.5 % fixed C. Industrial purity varies between 90 and 98 % carbon.

As refractory raw materials, the compositions, crystal structure and grain size of graphite have to be selected for refractories quality. Generally, the greater the flake size, the higher is purity, the better is quality of graphite. Ash composition of flake graphite contains mainly SiO_2, Al_2O_3 and Fe_2O_3, is a range between 40 ~ 70 %, 10 ~ 30 % and 10 ~ 30 % respectively. CaO and MgO contents are less than 10 % [18, 19]. In that respect, Stratmin's graphite ash composition is unique, having a CaO + MgO content of 30 % and 35 % SiO_2 only.

The structure of graphite is well known[20] (see Fig. 2), it indicates a planar structure with an infinite two dimensional array of carbon atoms arranged in hexagonal network in the form of a giant aromatic molecule. The carbon-carbon bond in the plane is stronger (the force in the same sheet is over 120 Kcal / atom-gram), as indicated by the interatomic distance of 1.42 °A, whereas the bonding between the planes is weak (the force between successive sheets is 20 Kcal / atom-gram), the interplanar spacing being 3.354 °A[18]. The planar structure results in marked anisotropic properties which is very important in the refractories application. The reference paper[22] reports that:

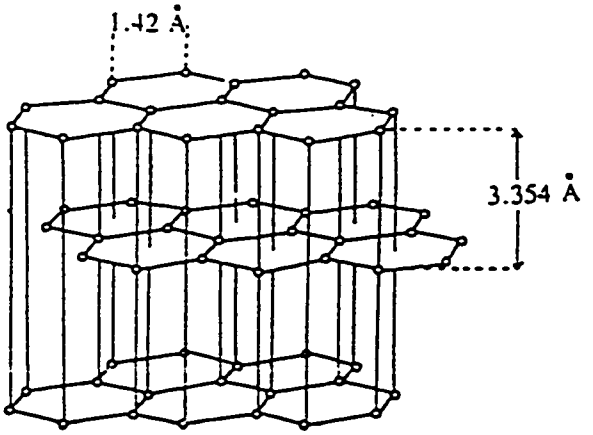


Fig. 2 Structure of flake graphite

1. thermal expansion perpendicular to the planes is 200 × that parallel to the planes.

2. thermal conductivity parallel to the planes is 200 × that perpendicular to the planes.

3. compressibility is 104 ~ 105 × greater in the direction perpendicular to the plane.

From refractory view point , properties of graphite should include coefficient of thermal expansion, thermal conductivity, compressibility[21] and the rate of oxidation.

However, degree of anisotropy decreases for a graphite component produced from a random array of graphite crystallites and properties of such a body can not readily be inferred from orientational factors in the random structure. The introduction of graphite in the refractory body is correlated with some properties related to the thermal shock resistance[23].

Natural flake graphite is widely used as a constituent in refractories designed to withstand molten slag and metals and thermal shock. Comparing with oxide refractories (no carbon), improvement of some properties of carbon containing materials is attributed to following properties of carbon:

a). lower thermal expansion. Cooper et al reported[24] that the contribution of the graphite crystal to the thermal expansion of refractories is almost negligible. This is probably due to the presence of cracks and porosity into which the graphite can expand. However, refractories containing a significant level of graphite (20 % by weight), will have a thermal expansion in the region of half that which might be expected from the oxide phase.

b). lower modulus of elasticity. The Young's modulus of graphite containing refractories is much lower compared with oxide refractories, attributed to the low surface energy between the graphite flakes and the matrix, also probably due to its poor bonding to the other phases.

c). higher work of fracture. Compared with oxide refractories, the work of fracture of graphite and oxide composites is higher, reaching in the case of mid alumina materials, values around of factor of 2 ~ 3. It is clear that the graphite can give a tortuous crack path and cause crack branching. It has the ability to absorb energy through basal plane slip. It can act as a plate-like reinforcement, absorbing energy either through pull-out or actual plate fracture.

d). higher failure strain. an additional favourable feature caused by the inclusion of graphite into refractories is that it gives rise to a high strain to failure. Cooper[16] has showed that the mean failure strain of these materials is in the range of 0.15 to 0.25 % at least, as evidenced by the ratio of flexural strength modulus. A similar expectancy for alumina-silicate refractories derived from the same ration is a range of 0.02 to 0.04 %. The implications of a high failure strain are that a very high thermal expansion which is beneficial to thermal shock resistance.

e). higher thermal conductivity. Thermal conductivity is introduced as a multiplier in the thermal shock resistance parameters. Graphite containing refractories are the most thermally conducting available because conduction in graphite is anisotropic, this can be built into refractories through textural variations and can be

utilized to an extent to transfer heat in preferred directions. So their excellent thermal shock resistance may also be partially explained by its property.

According to Cooper[16] the mechanical properties are more important than the thermal conductivity as such. The latter will have an influence in reducing the expansion stress though lower thermal gradients but probably no more so than in a highly conducting refractories.

The main drawback of carbon containing refractories is oxidation of carbon. At high temperature, carbon as bonding phase and graphite added to refractories are subjected to oxidizing gaseous environments provided by oxygen in the air , CO_2, water vapour, etc. The reactivity of carbon has been extensively studied, but in spite of the intensive efforts, certain details are not yet well understood. Part of the complications encountered in performing an analysis is due to the many factors which influence the rate of the gas-carbon reaction including microstructure, pore size and amount, crystallite size, degree of crystallinity, orientation, impurity content, surface area, etc. Other factors such as heat and mass transfer, have a significant effect on the kinetics of the reaction.

G. Doughty at al[25] reported that the reactions between graphite and an oxidizing gas are controlled by the following processes:

1). mass transfer of gaseous reactants from the bulk gas to the graphite surface.

2). adsorption of reactions.

3). reaction at the graphite surface.

4). desorption of reaction products.

5). mass transport of the gaseous reaction products away from the graphite surface.

The kinetics of the overall reaction will be governed by whichever of these is slowest. The rate determining step in the reaction is dependent upon the temperature, pressure, particle size of graphite, porosity, concentration of active sites for oxidation in the graphite and the concentration of catalytic impurities.

At low temperature(below 800 °C), rates of graphite oxidation are such that the rate controlling steps are steps 2, 3 or 4, particle size of graphite, active site concentration and catalytic impurity concentration are known to influence the reaction kinetics.

At high temperatures, the rate determining steps are the supply of gas to and from the reaction sites. In porous media, such as bricks, at intermediate temperatures, the rate is partially controlled by gaseous diffusion in the pores. At high temperatures, the reaction kinetics are controlled only by the diffusion of the gas to and from the external graphite surfaces.

Graphite containing refractories have long been recognized for their resistance to wetting by molten slags. Graphite, being a covalent material, has little affinity for oxide phases which when molten are primarily ionic in nature. With respect of some metals, a similar incompatibility of bond type results in a certain resistance to dissolution.

2.3 Binders

The following factors should be considered when choosing a binder for carbon containing refractories:

1). ability to wet grains and fines,

2). formability of the mixture with binder,

3). shelf time and ease in use,

4). properties of brick, such as strength and oxidation resistance,

5). pollution, minimal health risks,

6). price,

Carbonaceous binders developed from tar or pitch precursors have been used to bond basic refractories for a long history. Resin binders are popular in certain countries for environmental reason.

In this line, phenolic and furan resins have been used for various production of shaped and unshaped products[26], including for blast furnace taphole mixes, bricks made of doloma (magdoloma) -carbon, magnesia-carbon, slide gate components, etc. In the case of doloma, it is necessary to find the appropriate non-hydrous binder to cope with development of carbon bearing refractories.

Phenolic resins offer significant technical advantages, for example their suitability for flexible, low-polluting and energy saving mixing technologies (including cold-curing processes), and the thermal setting properties (dimensional stability) of cured semifinished products prepared with them. A relatively large fraction of binder carbon ("polymeric carbon") is formed when they are carbonized at temperature up to 1000 °C, the absolute quantity of which is depending on the type of resin, atmosphere and the

pyrolysis process[27]. Such resins are available as directly curable resole or as indirectly curing novolak systems which need an additional hardener (hexa–hexamethylene tetramine). They can be applied as fine powders, in liquid form, as solutions (containing organic solvents like furfural), as melts or in combinations of these systems. Depending on the type of binder to be used the preparation of the mixed bodies can be performed at ambient or only slightly increased temperature (directly curable resins which must not be heated up to more than about 50°C) or at elevated temperatures of up to 150°C (novolak melts, novolak solutions) [28].

The equally important factor to consider is the structure and properties of the carbon derived by pyrolysis of the resins, above 400 °C and up. This carbon called secondary carbon has a great influence on the properties of the refractories. Ideal resins have:

* high carbon yield

* good oxidation resistance

* strength throughout the temperature range

* low carbonization emissions (no potential carcinogens)

It has been found that properties such as carbon yield, graphitic character and oxidation resistance can be influenced primarily by two factors,

* the resin rheological properties (e.g. viscosity, reactivity, flow).

* the use of oxidation resistance modifier — a further modification which enhances the oxidation resistance by chemical means rather than structural changes.

P. Williams et al[29] have shown the relationship between two of these parameters and a property of a cured novolak / hexamine composition, mainly the oxidation resistance. Suitable ranges of properties can be selected, and the resin with the specific properties synthesised. They[19] have shown that maximum resistance to oxidation is obtained with low resin viscosity, easily "graphitized" at high temperature.

A relative ranking of organic binder properties for the main resin types and pitch is shown in Table 2[29,30].

Table 2. Relative ranking of organic binder properties

Characteristic	Resole	Novolak	Pitch
green strength in wide temperature range	good	good	poor
wetting ability	good	good	good
shelf time	poor	good	moderate
safety in use	moderate	moderate	poor
ease of handling	good	good	poor
carbon yield	good	good	good
porosity size	micro.	micro.	macro.
oxidation resistance	moderate	moderate	good
strength at elevated temperature	good	good	poor
thermal shock resistance	poor	poor	good
thermal conductivity	similar	similar	similar
carbonization emissions	moderate	moderate	poor

2.4 Additives for Oxidation Resistance

For the purpose of carbon protection, it is necessary to use additions as antioxidants. The additives for oxidation resistance will be divided into two broad classes: metallic and non-metallic, and subdivided further into categories, including one or several metals and / or alloys, carbides, borides, nitrides, fine oxides and glasses. M. Rigaud [31] have reviewed the subject in details concentrating on metallic antioxidants (Al, Mg, Si and alloys) and new additives (silicon carbide and borides). In this review, only boron compounds additives will be considered.

Boron bearing materials , such as B_4C, CaB_6, ZrB_2 and TiB_2, are synthetic products, they can be produced by a variety of techniques. For economic reasons, however , only three of the techniques are used commercially[32]:

* Carbothermal reduction

B_4C: $B_2O_3 + C \rightarrow B_4C + CO$ [2--1]

Metal borides (MB_n): $MO_n + B_2O_3 + C \rightarrow MB_n + C$ [2--2]

* Metallothermal process

B_4C: $B_2O_3 + C + Al\ (Si, Mg) \rightarrow B_4C + (CO) + Al\ (Si, Mg)\ oxide$ [2--3]

Metal borides (MB_n):

$MO_n + B_2O_3 + Al\ (Si, Mg) \rightarrow MB_n + Al\ (Si, Mg)\ oxide$ [2--4]

* Boron carbide process (only metal borides):

$MO + B_4C\ (+ C) \rightarrow MB_n + CO$ [2--5]

1). B_4C

Crystal structure of B_4C is rhombohedral, specific gravity: 2510 kg/m^3 ,melting point: 2450°C, maximum use temperature: in oxidizing atmosphere — 800°C; in inert atmosphere — 2200°C[32]. The mechanism by which B_4C functions as an antioxidant is the most thoroughly studied of all boron compounds. Attention has focused particularly on the interaction of B_4C and MgO-C. T.R.Lipinski et al[6,7,33] have demonstrated that B_4C is oxidized at temperature below 1000°C according to the following reaction equations:

$$B_4C_{(s)} + 3O_{2(g)} \rightarrow 2B_2O_{3(l)} + C_{(s)} \qquad [2\text{--}6]$$

$$B_4C_{(s)} + 6CO_{(g)} \rightarrow 2B_2O_{3(l)} + 7C_{(s)} \qquad [2\text{--}7]$$

then, B_2O_3 react with MgO to form a magnesium borate ($Mg_3B_2O_6$) :

$$3MgO_{(s)} + B_2O_{3(l)} \rightarrow Mg_3B_2O_{6(l)} \qquad [2\text{--}8]$$

The magnesium borate melt generated does poorly wet carbon particles, but wets MgO grains well. The protective mechanism to carbon is explained by the formation of a continuous network linking MgO grains with magnesium borate bridges. This structure can effectually seal the surface of the brick and prevent the oxygen access to carbon. At temperature above 1300°C, the magnesium borate reacts with carbon to form Mg vapor and B_2O_3 gas,

$$3Mg_3B_2O_6 + 4C \rightarrow 3\,Mg_{(g)} + B_2O_{3(l)} + 4\,C \qquad [2\text{--}9]$$

According to M.Rigaud et al[34], the same gaseous products also might be formed by the reaction of MgO with B_4C,

$$6MgO + B_4C \rightarrow 6\,Mg_{(g)} + 2\,B_2O_{3(g)} + CO \qquad [2\text{--}10]$$

It has also shown[34] that B_4C is indeed an efficient anti-oxidant for doloma-carbon material, in the critical temperature range of 1000°C to 1600°C. The rationale of the oxidation resistance is similar with MgO–C with B_4C. The difference is that in doloma–carbon material CaO preferentially reacts with B_2O_3 to form $Ca_3B_2O_6$.

2). CaB_6

CaB_6 belong to cubic crystal structure, specific gravity: 2450 kg /m^3; melting point: 2185°C; maximum use temperature: 700°C (in oxidizing atmosphere) and 2000°C (in inert atmosphere) [32] . K.Watanabe[35] has reported that in the MgO–CaB_6 system, reaction first proceeds according to the following equation:

$$10\,MgO + CaB_6 \rightarrow 10\,Mg_{(g)} + 8/3\,B_2O_{3(l)} + Ca_3B_2O_{6(l)} \qquad [2\text{--}11]$$

The surplus B_2O_3 can continue to react with MgO matrix, so that the following total reaction may be expected:

$$18\,MgO + CaB_6 \rightarrow 10\,Mg_{(g)} + 1/3\,Ca_3B_2O_{6(l)} + 8/3\,Mg_3B_2O_{6(l)} \qquad [2\text{--}12]$$

These reactions are confirmed by T. R. Lipinski [36] with TGA test. In this work [36], a mixture of 100 parts MgO (seawater clinker, < 0.1mm) and 5 parts CaB_6 are available for the test. The measurements are made on powder specimens in an argon atmosphere up to a maximum temperature of 1500°C (for 5h). A decrease in weight may be

observed from approx. 1300°C. Final weight loss (11.26 %) is in very good conformity with theoretical weight loss in reaction [12] of 11.03 %. After the TGA test, XRD analysis shows definite amounts of $Mg_3B_2O_6$ and $Ca_3B_2O_6$, no more CaB_6 could be detected.

Hanagiri[37] have studied effect of mixed additive of CaB_6 and Al powder on properties of MgO–carbon brick and obtained noticeable improvement of properties, not only for oxidation resistance, but also for spalling resistance and hot strength, hot strength at 1400°C being improved to proximately 1.5 times.

3). ZrB_2

The characteristics of ZrB_2 are: hexagonal crystal structure, specific gravity: 6090 kg/m^3, melting point: 3262°C; maximum use temperature in oxidizing and in inert atmosphere: 800°C and 2400°C respectively[32] .

Studies on refractory properties of ZrO_2 were initiated in Japan. Kuwabara[38] have developed ZrB_2 containing bricks and castables with different ZrB_2 amounts. Yamaguchi et al [39,40] have studied the behavior of oxidation resistance of ZrB_2 in MgO–carbon and carbon bricks and concluded that ZrB_2 can improve oxidation resistance of these refractories between 700°C and 1200°C. ZrB_2 react with oxygen at low temperature:

$$ZrB_2 + 5/2\ O_{2(g)} \rightarrow ZrO_{2(s)} + 2\ B_2O_{3(l)} \qquad [2\text{--}13]$$

ZrB_2 coexisting with carbon reduces CO (formed from oxidation of C) to C according to the following reaction:

$$ZrB_2 + 5CO_{(g)} \rightarrow ZrO_{2(s)} + B_2O_{3(l)} + 5C_{(s)} \qquad [2\text{--}14]$$

and thus decreases oxidation loss of carbon. Furthermore, the B_2O_3 formed will react with refractory oxides to form MgO–B system liquids phase protective layer which further inhibit oxidation of carbon.

4). TiB_2

The characteristics of TiB_2 is similar with ZrB_2. TiB_2 reacts with oxygen to form TiO_2 and B_2O_3. The TiO_2 formed will continue to react with refractory oxides to form titanate compounds which will be beneficial to improvement of oxidation resistance and thermal shock resistance. However, up to now, development of TiB_2 in practice application has been restricted to small proprietary effects on few refractories products[32].

5). Mg–B Material (Bc)

Mg–B material is a proprietary combination of elemental boron with magnesia and oxygen[41]. In recent years, the reports on research conducted independently in North and South America and Japan have consistently shown that this material enhances the physical properties as well as the anti-oxidation characteristics of MgO–carbon refractories[42-44]. Comparing oxidation behavior of Mg–B and B_4C, the results of oxidation tests are illustrated in Fig. 3[45].

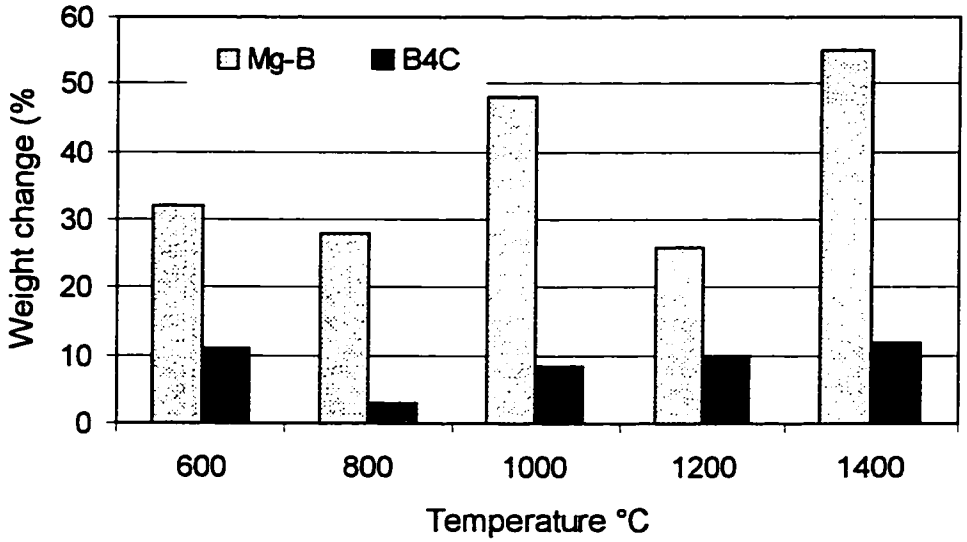


Fig. 3 Results of oxidation test of Mg–B and B_4C

It can be seen from the Fig. 3 that weight gain changes of Mg–B material at each testing temperature is larger than that of B_4C. Accordingly, it is recognized that Mg–B material have higher affinity with oxygen, e.g. the Mg–B material reacts more easily with O_2 than B_4C.

An investigation [44] on properties of MgO–carbon brick, used as a tap-hole with Mg–B addition and Al (or Al–Mg alloy) powder has resulted in improved hot strength at 1400°C and oxidation resistance. The properties of the tap hole brick is shown in Table 3 .

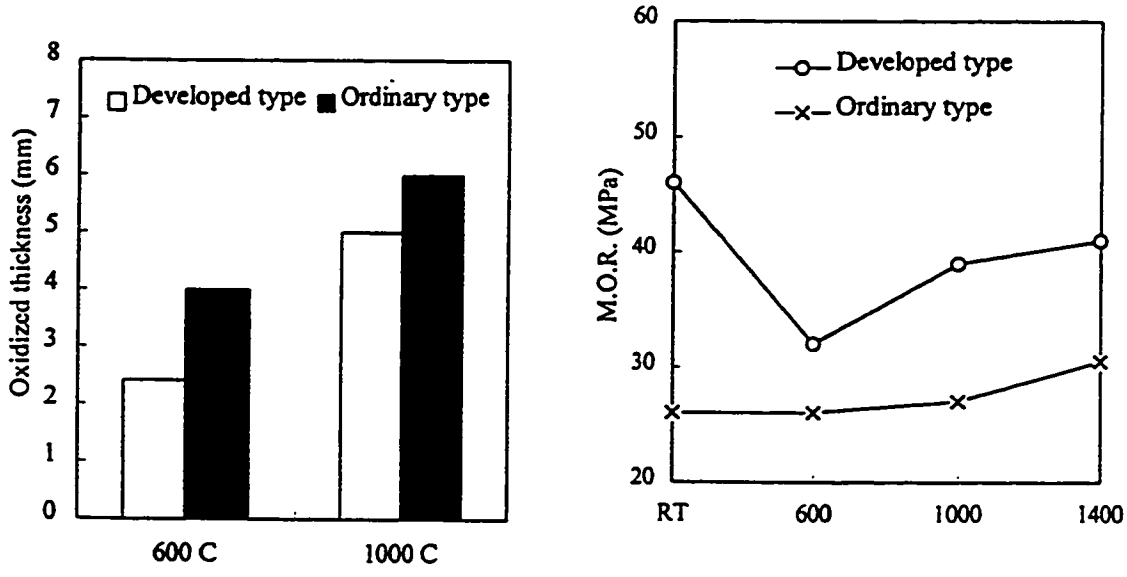
Table 3. Properties of MgO–C top hole brick

	Ordinary type	Improved type
Service life	175 heats	200 heats
Fused MgO	O	O
Graphite	O	O
Metal additive	O	O
Mg–B additive	--	O
Chemical composition: MgO	79.5	79.7
(%) F. C.	17.3	17.2
Bulk density (g/cm^3)	2.97	2.98
Apparent porosity (%)	1.6	1.1
Cold crushing strength (MPa)	57.5	61.2
Hot modulus of rupture (MPa), (at 1400°C)	15.9	16.9
Corrosion index	100	84

K. Ichikawa [45] has studied oxidation resistance and hot strength of Al_2O_3 –carbon sliding plates with the two kinds of additives, Mg–B material and B_4C respectively. Chemical and physical properties of the Al_2O_3–carbon sliding plates are listed in Table 4. Results of oxidation test and HMOR measurements are shown in Fig. 4 -a and b.

Table 4. Chemical and physical properties of sliding plate bricks

Properties		Developed type	Reference type
Chemical composition: (%)	Al_2O_3	84	
	ZrO_2	3	
	C	5	
Additives:	Al	O	O
	Mg–B	O	--
	B_4C	--	O
Apparent porosity	(%)	9.5	11.6
Bulk density	(g / cm^3)	3.14	3.15
C. C. S.	(MPa)	195	155
C. M. O. R.	(MPa)	49.0	29.2



(a) (b)

Fig. 4 Results of oxidation (a) and hot strength (b) tests on Al_2O_3–C sliding plate brick

The results show that Mg–B additive has noticeable effects on both anti-oxidation and strength of MgO–carbon and Al_2O_3–carbon refractories.

6). AlB_2

Experimental study of H. Sunayama et al [46] on MgO–carbon brick with AlB_2 additive exhibit better applicable prospects of AlB_2, (see Fig. 5). In this work, oxidation rate of MgO–C brick added with AlB_2 was measured in air at 1400°C for 6 hours. Result of this study shows that with increase of AlB_2 content from 1% to 2 %, decarbonization area is decreased, and the sample with 3 % AlB_2 has better oxidation resistance. Compared with no AlB_2 specimen, decarbonized area of the specimen with 3 % AlB_2 is decreased abruptly from 100 % to 31% after heating to 1400°C for 6 hours, and total porosity of the specimens decreases from 28 % to 12.1%. Furthermore, with increase of AlB_2 content from 0 to 3%, amount of large size pores (> 10 μm) is decreased remarkably. XRD analysis shows that new mineral phases formed in the undecarbonized region are Al_4C_3 and $MgO{\cdot}Al_2O_3$ spinel and in the decarbonized region are $Mg_3B_2O_6$ and $MgO{\cdot}Al_2O_3$ spinel.

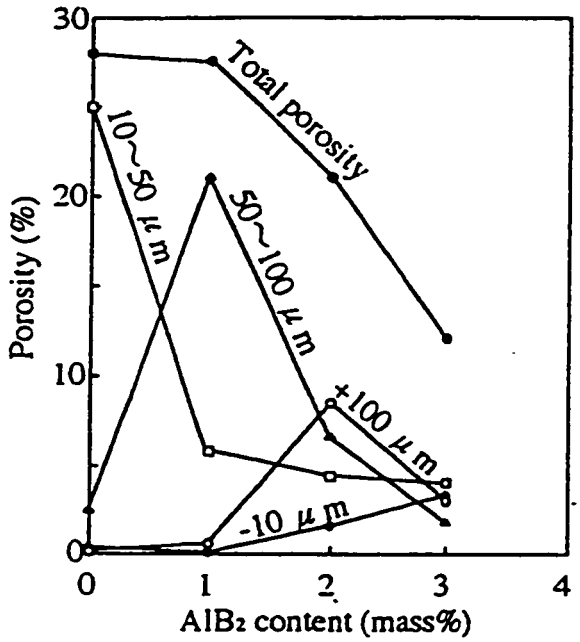


Fig.5 Effect of AlB_2 content on porosity classified by pore size of MgO–C refractories after heating at 1400°C for 6h [46]

7). $Al_8B_4C_7$[47,48]

$Al_8B_4C_7$ is a complex compound with composition of Al_4C_3 : B_4C = 2 : 1 (mol ratio). Its melting point is reported to be 1900°C. After mixed powder with composition of Al : B : C = 8 : 4 : 7 is fired in argon atmosphere at 1700°C, the $Al_8B_4C_7$ will be obtained. $Al_8B_4C_7$ as an anti-oxidant for Al_2O_3–C and MgO–C materials reacts with CO to form Al_2O_3 and B_2O_3,

$$Al_8B_4C_7 + 18\ CO_{(g)} \rightarrow 4\ Al_2O_3 + 2\ B_2O_{3(l)} + 5C_{(s)} \qquad [2\text{--}16]$$

Al_2O_3 and B_2O_3 further react with each other to form liquid phase. The liquid phase forms protective layer on surface of refractories and thus inhibits oxidation of carbon. In

addition, hydration resistance of $Al_8B_4C_7$ bearing refractories is excellent and sufficient for practical application .

8). BN

Boron nitride has also been studied as an anti-oxidant. It has been shown by H. Zhao et al [49] that BN oxidizes in the range of 1000 ~ 1200°C. Like many of the previous boron containing compounds, the cost of BN is a major factor, limiting its usage.

2.5 The Characteristics of MgO–CaO–C Refractories

In MgO–CaO–C refractories, the main constituents MgO and CaO, have extremely high melting points, 2800 °C and 2570 °C respectively, and also have high eutectic temperature, 2370 °C [13].

The thermal expansion coefficient of CaO is lower than that of MgO, so it is beneficial to thermal shock resistance.

In comparison with MgO, vapor pressure of CaO at high temperature is lower, CaO is more stable thermodynamically when it contacts with carbon. As shown in Fig. 6[50], the lines for free energy of formation of MgO and CaO intersect with the line of CO at 1850 °C and 2180 °C respectively, at which Mg vapor of 1 atm., and CO of 1 atm., Ca vapor of 1 atm. and CO of 1 atm will be produced respectively. From this point, carbon bonded CaO bearing material may be used at higher temperature than MgO–C bricks.

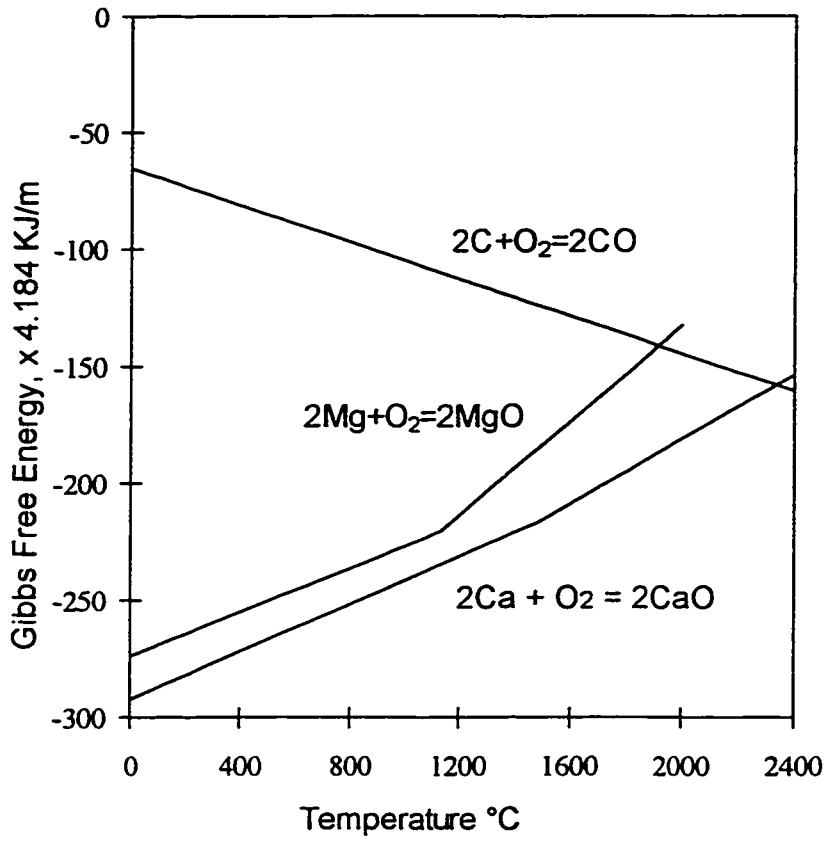


Fig. 6 Equilibrium relations for magnesium oxide, lime and carbon monoxide

Free CaO existed in bricks will preferentially react with SiO_2 in slag, to form minerals with high melting point, C_3S (2070 °C) and C_2S (2130 °C).

Y. Naruse et al have reported [51] that with magdoloma-carbon bricks used at sidewalls and bottom areas of a 150-ton BOF, it was possible to slow down the wearing rate by 20 ~ 30 %, compared with magnesia-carbon brick (see Fig. 7).

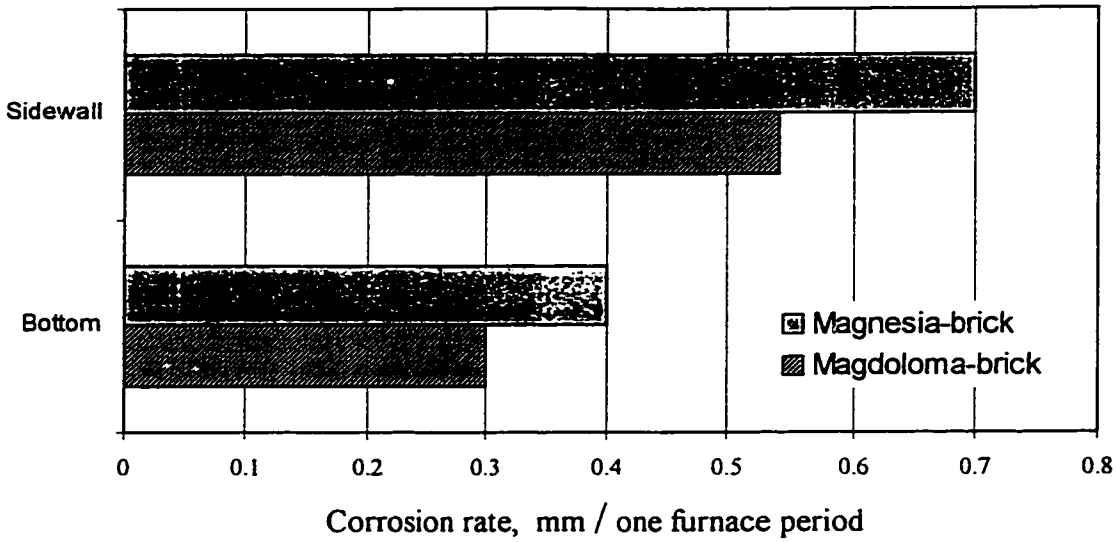


Fig. 7 Comparison of corrosion rate between magnesia-C and magdoloma-C bricks in BOF[51]

Schruff et al have reported [52] that in clean steel technology, steel casting ladles lined in molten steel bath area, with resin-bonded doloma bricks have better service results. Fig.8 (a) shows the influence of various refractory lining on the deoxidation and the desulphurization of molten steel in a induction furnace with 50 Kg capacity at 1600°C under argon [53]. Al loss is smaller in the case of lime or doloma bricks. Besides, a series of laboratory experiments with synthetic lime-periclase refractories have been conducted by Degawa et al[54] in order to investigate the influence of MgO : CaO ratio on desulphurization efficiency. In the range of MgO contents from 0 to 70 %, it is shown that desulphurization rates are highest for compositions between 30 and 50 % MgO, (see Fig. 8-b). This means that the naturally occurring doloma has an ideal composition from the point of view of desulphurization.

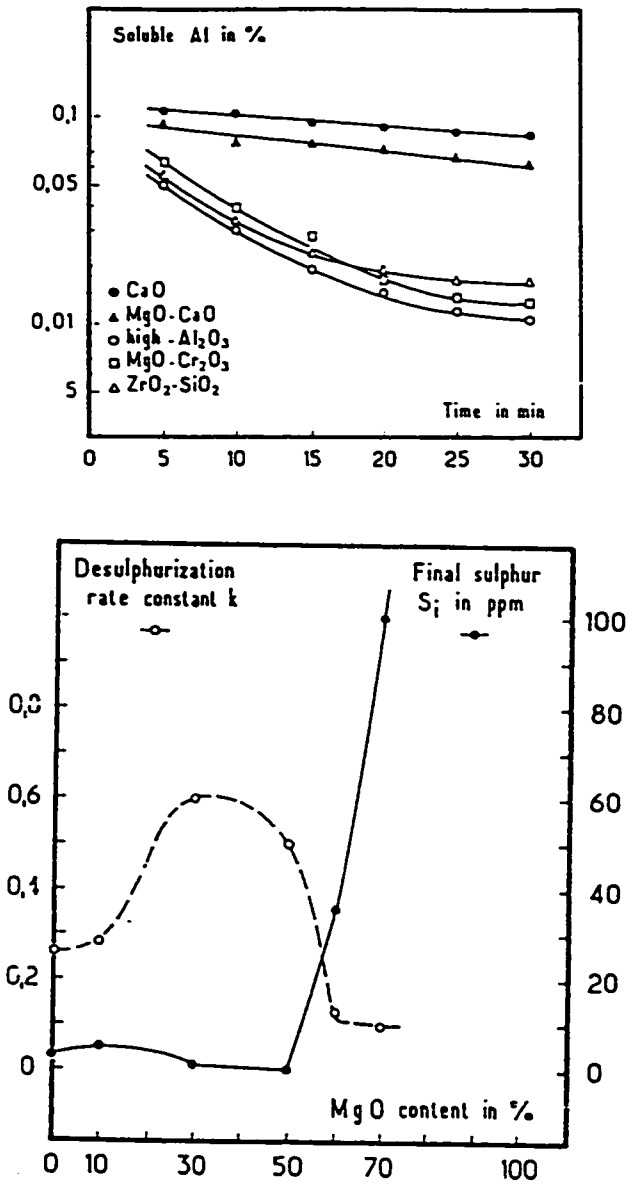


Fig. 8 Influence of the ladle lining on deoxidation (a) and desulphurization (b)[53]

CHAPTER 3. THE MAKING OF DOLOMA-C AND MAGDOLOMA-C SPECIMENS

This chapter will introduce starting materials (raw materials, additives and binder), formulations of specimens and preparation of specimens used in our tests.

3.1 Definition of the Materials Used

3.1.1 Raw Materials

(A). Doloma (dead–burned dolomite clinker)

The doloma used in the experimental work is a dead-burned high purity dolomite clinker recognized as a good refractory grade doloma. Its chemical composition and physical properties are listed in Table 5. The grain sizes used in this work were: 3 ~ 7, 7 ~ 14, 14 ~ 30, 30 ~ 60, 60 ~ 0 and < 200 mesh.

(B). Magdoloma (dead-burned magdolomite clinker)

The magdoloma clinker used is a synthetic product made from light-burned magnesite and lime by a two-stage calcination process[12]. Its chemical composition and physical properties are also listed in Table 5. The grain sizes are the same as for doloma in above (A).

Table 5. Chemical and Physical Properties of the Doloma and Magdoloma clinker

Composition (%)	Dolomite	Magdolomite
MgO	41.0	71. 10
CaO	57.0	25.50
Fe_2O_3	1. 0	0. 90
SiO_2	0.6	1. 27
Al_2O_3	0.4	0.76
Bulk Density (g / cm^3)	3.25	> 3.25

(C). Graphite

The natural flake graphite used has more than 96 % purity and an average grain size of < 100 mesh. The chemical composition of its ash is given in Table 6 analyzed by XRF.

Table 6. Chemical composition of graphite ash (wt %)

SiO_2	Al_2O_3	Fe_2O_3 (total)	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_3	SO_3	L.O.I. 1100°C
37.3	9.69	12.0	8.9	20.9	1.46	2.23	0.38	0.12	0.12	1.67	4.63

3.1.2 Antioxidants

The antioxidants include: (1). Four distinct boron bearing compounds— ZrB_2, CaB_6, Bc (an Mg-B material) and Colemanite. (2) two metallic additives — Al-Mg alloy or Al powder.

1). CaB6

CaB6 used is a commercial product with greater than 98 % purity, in the form of a dark powder, less than 44 μm. Its calcium content is about 39 wt %.

2). Bc

Bc is a commercial product composed of elemental boron, magnesium and oxygen. It has a composition of about 60 wt % boron and 40 wt % oxide compounds . After oxidation, this material is identified by X-ray powder diffraction analysis[45] as $3MgO:B_2O_3$ (Kotoite).

The average particle size of the Bc used is about < 20 μm.

3). ZrB2

Zirconium diboride used is a synthetic product with greater than 98 wt % purity. Its zirconium content is about 83 wt %. It is a gray powder, less than 44 μm.

4). Colemanite

The colemanite is a borate minerals having theoretical formula $2CaO \cdot 3B_2O_3 \cdot 5H_2O$ with 50.9 % B_2O_3 content. Chemical composition of the mineral used is shown in Table 7. In our experimental work, DTA has been carried out to determine the temperature of decomposition of crystalline water in colemanite, which is found to be 340 ~ 400 °C as shown in Fig. 9. Therefore, the colemanite used in this work is dewatered at 450 °C for 10 hours. After this, it is ground to 44 μm for use.

Table 7 Chemical composition of colemanite, as provided

Compositions	Minimum (%)	Maximum (%)
B_2O_3	40.00	42.00
CaO	23.50	24.50
Total Sulphur	0.40	0.60
Fe_2O_3	0.40	0.55
Al_2O_3	2.30	2.60
MgO	1.40	1.70
K_2O	0.03	0.06
Na_2O	0.01	0.02
Cl	0.05	0.07

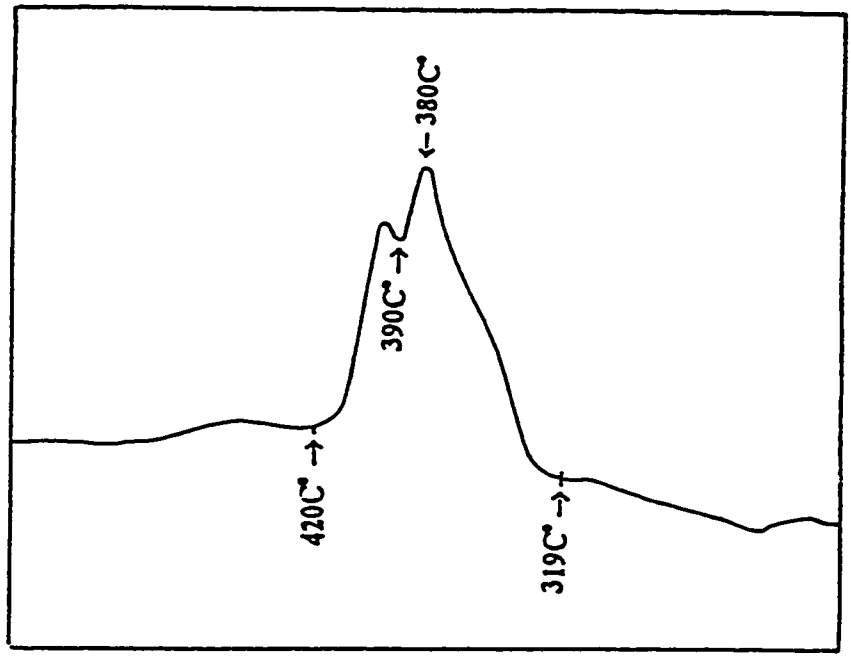


Fig. 9 The differential thermal analysis of colemanite

5). Al-Mg alloy

The Al-Mg alloy powder has composition of Al : Mg = 50 : 50 and an average particle size of about < 20 μm. The aluminum powder has a > 99 %purity.

3.1.3 Binder

Liquid non-hydrous resin and solid resin are used as binders. Liquid one is a heat reactive phenolic resin of one-step type. Its physical properties are as following:

Viscosity,	(25°C)	2900 CPS
pH,	(25°C)	6.2 ~ 6.7
Water,	(%)	0.052
Phenol,	(%)	1.6

Solid resin is a finely pulverized, high molecular weight, novolac resin which contains hexamine 7.8 %. Its hot plate cure time at 150°C is 60 ~ 90 seconds and particle size is less than 200 mesh.

3.2 Specimen Formulations

Three series of doloma(carbon specimens with boron bearing additives and two set of magdoloma-carbon specimens with boron bearing additives have been prepared for investigations. For comparison, reference specimens of doloma-carbon and magdoloma-carbon specimens without additive (DO and MDO) and with metal additive (DA and MDA) have also been prepared.

The formulations of the base materials of doloma-carbon and magdoloma-carbon specimens without additive (DO and MDO) are shown in Table 8-a.

Table 8-a. The formulations of the base materials of doloma-C and magdoloma-C specimens without additive (DO, MDO)

Grain Size proportion	%
4 ~ 6 Mesh	20
6 ~14	35
14 ~30	10
< 60	5
< 200	20
Graphite	10
Resin (liquid)	4
(solid)	1

3.2.1 Doloma-Carbon Specimens

1). Series I — containing ZrB_2, CaB_6, Bc (4 % each) and Colemanite (5 %), (specimen code: DZ, DC, DS and DB).

2). Series II — containing varying amount (2, 3, 4 %) of CaB_6, ZrB_2 and Bc (specimen code: DC DZ and DS).

3). Series III — (a). Doloma-carbon specimen with fixed ratio (2 : 2) of boron bearing additives (CaB_6, ZrB_2 and Bc) and Al-Mg alloy, specimen code: DCA, DZA

and DSA. (b). Doloma-carbon specimen with varying Bc / alloy ratio (ratio: 2:2, 1:2, 0.5:2, 1:3 and 0.5:3).

The addition formulations for the three series of doloma-carbon specimens are given in Table 8-b.

Table 8-b. Formulation of the three series of doloma-C specimens

Speci. code	CaB_6	Bc	ZrB_2	Colemanite	Mg-Al alloy
DC*	4	-	-	-	-
DS*	-	4	-	-	-
DZ*	-	-	4	-	-
DB	-	-	-	5	-
DA	-	-	-	-	4
DCA	2	-	-	-	2
DSA	-	2	-	-	2
DZA	-	-	2	-	2
DSA 1:2	-	1	-	-	2
DSA 0.5:2	-	0.5	-	-	2
DSA 1:3	-	1	-	-	3
DSA 0.5:3	-	0.5	-	-	3

* 2 and 3 % additions in series II of specimens

3.2.2 Magdoloma-Carbon Specimens

The formulations for magdoloma-carbon specimens are given in table 8-c.

Table 8-c. The addition formulations of magdoloma-C specimens

Specimens No.	Additives
MDC	CaB_6 4 %
MDS	Bc 4 %
MDZ	ZrB_2 4 %
MDA	Alloy 4 %
MDCA 2:2	CaB_6 2 % + alloy 2 %
" 1:2	" 1 % + " 2 %
" 0.5:2	" 0.5% + " 2 %
" 0.5:3	" 0.5% + " 3 %
" 1 : 3	" 1 % + " 3 %

3.3 Preparation of Specimens

The starting materials are mixed and blended uniformly according to the formulations described above, after which the mixes are hydraulically pressed under 180

MPa. The experimental bars (203.5mm × 51mm × 51 mm) formed are heat-treated at 180 °C for 15 hours. Finally, they are cut to the following sizes for tests:

(1). 51mm × 51mm × 51mm for oxidation tests in box furnace and slag corrosion tests with crucible method (drilled in hole)

(2). 203.5mm × (51mm/ 38mm) × 38 mm for rotary oxidation tests and rotary slag corrosion tests.

(3) . 125mm × 25mm × 25mm for HMOR tests.

The physical properties of the principle specimens investigated in this work are shown in Table 9.

Table 9. Physical properties of experimental bars

No. of specimens	Apparent Porosity (%)		Bulk Density (g/cm^3)		CMOR (MPa)
	Before Carbonization	After Carbonization	Before Carbonization	After Carbonization	No Carbonization
DO	3.10	12.70	2.78	2.68	14.71
DA	4.06	12.22	2.72	2.67	16.68
DB	6.85	16.63	2.64	2.57	11.74
DZ	4.20	11.90	2.81	2.74	14.54
DS	5.09	11.13	2.71	2.69	12.29
DC	4.66	12.02	2.71	2.67	13.63
DZA	4.05		2.84		17.57
DSA	4.56		2.79		14.57
DCA	4.15		2.80		15.22
MDC	4.09	12.28	2.73	2.70	15.73
MDCA	3.27	12.48	2.75	2.69	15.50
MDS	4.27	12.57	2.73	2.69	17.34
MDZ	3.71	12.54	2.78	2.73	15.43
MDA	4.16	13.15	2.72	2.68	15.93
MDO	3.63	13.93	2.76	2.70	16.47

CHAPTER 4. EXPERIMENTAL PROCEDURE

In this chapter the following testing methods are described for: 1). oxidation tests; 2). slag corrosion tests; 3). hot modulus of rupture tests.

4.1 Oxidation Tests

The two oxidation test methods adopted in this work are: (1). box furnace (at 1200°C and 1400°C); (2). rotary furnace (at 1600°C). After oxidation, phase composition and microstructure of oxidized layer of specimens are analyzed by XRD and SEM.

4.1.1 Oxidation Tests in Box Furnace

Cubic samples of 50mm × 50mm × 50 mm cut from the experimental bars (without carbonization treatment) are oxidized in a box furnace in air. Oxidation is performed in air at 1200°C and 1400°C for 3 hours (not including the time periods of heating and cooling). In order to minimize error of the experimental data, the testing conditions, (such as test temperatures and time; heating and cooling rate; sample position in furnace etc.) are carefully controlled and kept as identical in all tests. After oxidation, the samples are cut in half. The depth of the oxidized layer is measured on the cut-surfaces of samples (measured at nine points for each sample) and their average value is calculated. The weight changes after oxidation tests are also measured.

4.1.2 Oxidation Test in Rotary Furnace

The specimens cut from experimental bars have a sizes of 203.5mm × (51mm/ 38 mm) × 38mm. The experimental set-up (furnace configuration and specimen geometry) of dynamic rotary test furnace is shown in Fig. 10. In this test, six specimens without carbonization treatment (one specimen from each type of experimental bars) are simultaneously oxidized. The combustion gases are gas and oxygen. The rotary speed of the furnace is 3 rpm. The temperature of hot face in furnace is measured using an optical pyrometer. After reaching the test temperature 1600 °C in about 1.5 hours, the testing bricks are held at this temperature for 6 hours, and left to cool back to room temperature. The specimens are then removed from the furnace, and sectioned in half in a perpendicular direction to hot surface. The oxidation behavior is evaluated by measuring the depth of decarbonized layer only.

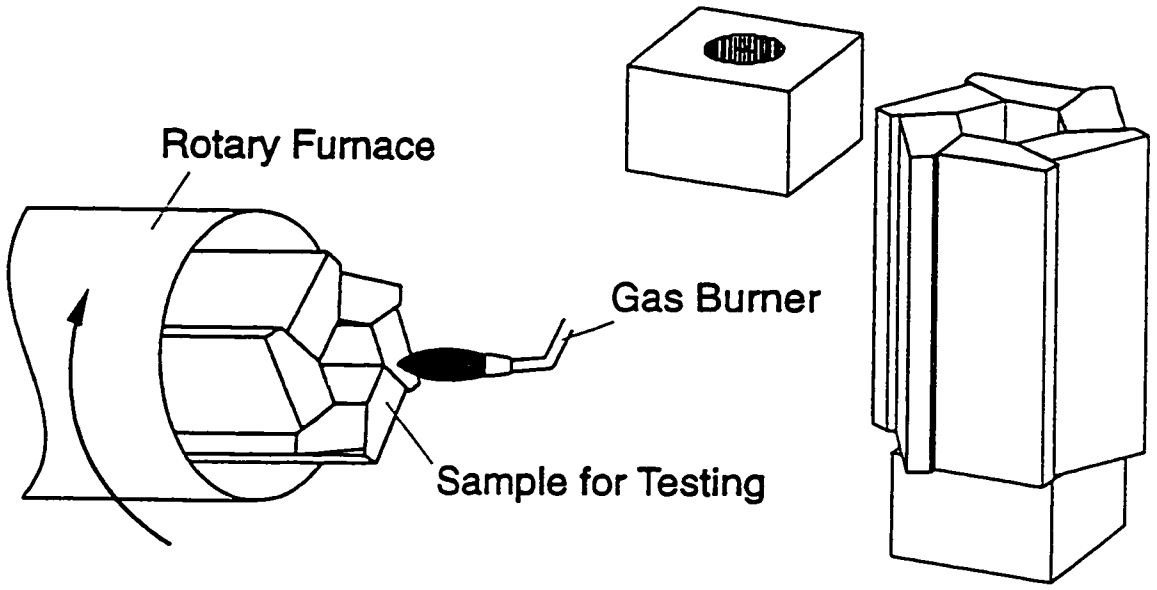


Fig. 10 Experimental set-up for oxidation test in rotary furnace

4.2 Slag Corrosion Resistance Tests

Slag corrosion tests are carried out by two methods — (1). rotary method (dynamic test, ASTM standard C874–85), and (2). crucible methods (static test). After corrosion tests, XRD and SEM are used for analysis on phase composition and microstructure of residual specimens.

4.2.1 Rotary Test Method

The experimental set-up and specimen sizes for rotary corrosion resistance test is similar to that for oxidation test described above (Fig. 10). Rotary speed of the furnace is 3 rpm. The testing temperature is set at 1600°C and held on at this temperature for 10 hours. Surface of specimens in furnace is heated to 1600°C and hold on for half hour, then, steelmaking slag is fed at 30 minutes intervals (200g slag each charge, but 400g slag in first charge); in total 4 kg slag is charged for each test. After the test, the specimens are cut in half in a direction perpendicular to corroded surface along the length. Corroded thickness and depth of reaction zone are measured for evaluation of corrosion behavior.

4.2.2 Crucible Method

Holes (diameter 25mm, depth 30mm) are drilled in the center of cubic specimens (51mm × 51mm × 51mm) cut from experimental bars. The hole is filled with 30g of slag. Six crucible specimens are put into a box made of fused magnesia. The space

around crucible specimens in the box is filled with graphite. Top surface of crucible specimens is exposed to air in order to simulate practical service conditions in lining (see Fig. 11). Then, the box with six specimens (one crucible from each type of experimental bar) is fired to 1600°C and held on this temperature for 3 hours in box furnace in air. Then, the crucible specimen are cooled in the furnace to room temperature, the specimens are then cut in half, from top to bottom in the center of the hole. Finally, corroded thickness and depth of reaction zone is measured for evaluation of corrosion behavior.

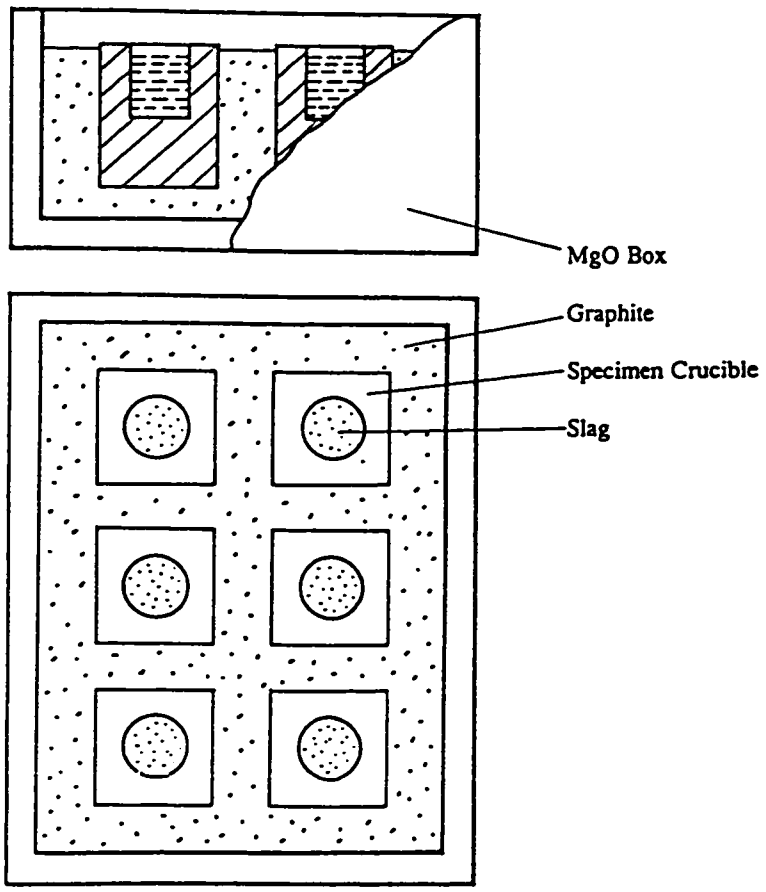


Fig. 11 Illustration of crucible method for slag corrosion test

4.3 Measurements of Hot Strength

Modulus of rupture at different temperature is determined by the conventional three point bending method under controlled reducing atmosphere.

The specimen dimensions used for the strength tests are 120mm × 25mm × 25 mm. They have tested without carbonization treatment. Six bar specimens are tested in one run. The specimen bars are put into a SiC-Si_3N_4 box with a bottom slide plate and covered with graphite to prevent oxidation. The position of the specimens in the box is shown in Fig. 12. The box is then put into the furnace for HMOR testing. For this test, the equipment used is automatically controlled by computer. All testing conditions, such as temperature rise; soaking; loading; sample feeding and stopping; record and printing testing date; error warning; load calibration, are controlled carefully.

HMOR value of specimens is calculated by following formula:

$$Re = \frac{3}{2}\frac{LF_{max}}{bh^2}$$

where: Re ---Modulus of rupture (MPa)

L --- The span between the lower support points (mm)

F --- Maximum load (N)

b --- The width of specimen (mm)

h --- The height of specimen (mm)

After the HMOR tests, mineral phase and microstructure of the specimens are analyzed by XRD and SEM.

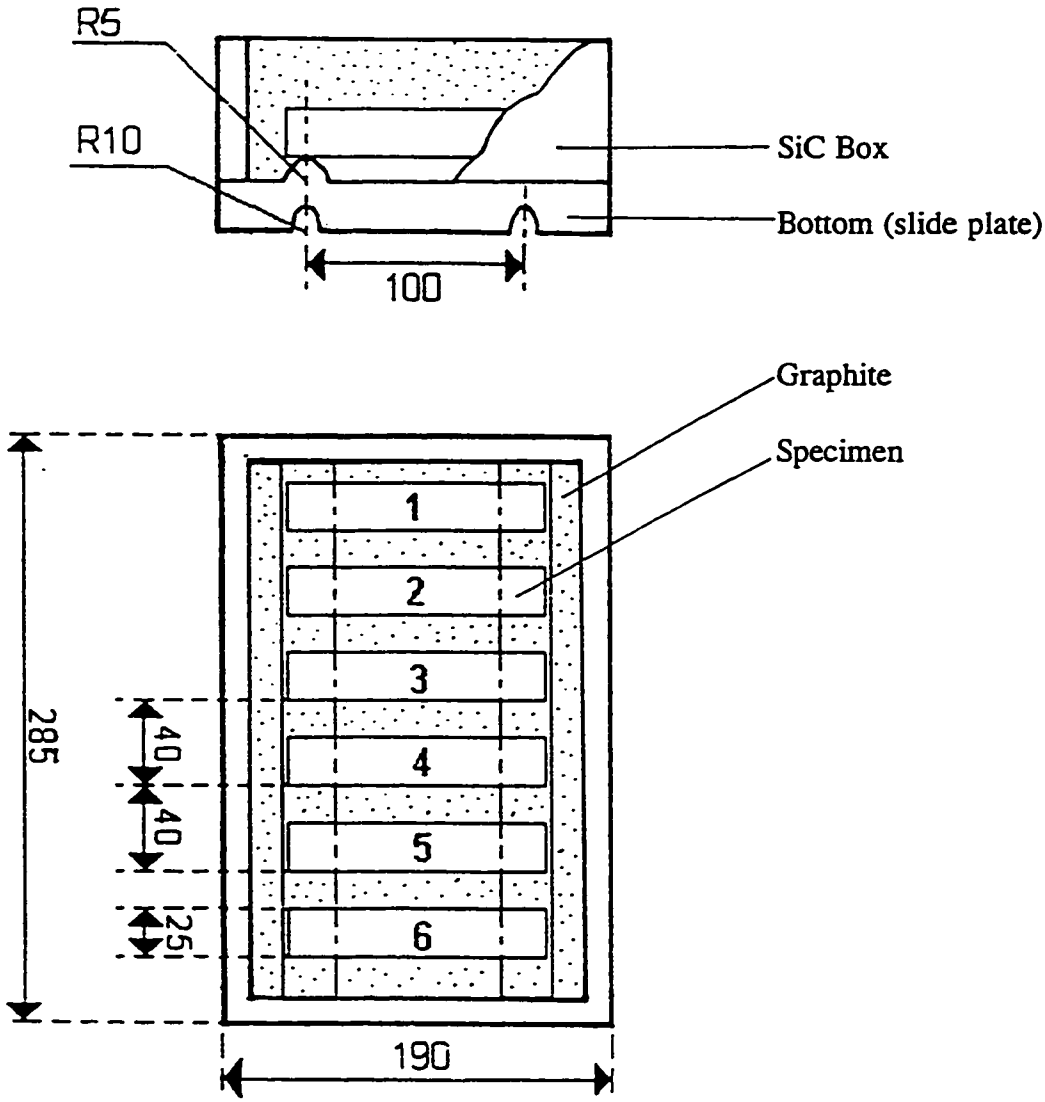


Fig. 12 Illustration of HMOR specimens in the furnace

CHAPTER 5. OXIDATION RESISTANCE OF DOLOMA–CARBON AND MAGDOLOMA–CARBON REFRACTORIES

Three series of doloma-carbon specimens and one set of magdoloma-carbon specimens with boron bearing additives have been investigated for oxidation behavior in comparison with corresponding specimens without additive and with Mg–Al alloy additive only. The formulations and properties of these specimens are given in Chapter 3 and testing methods (box furnace and rotary furnace) are described in Chapter 4.

5.1 Oxidation Tests of Doloma-Carbon Materials

5.1.1 Effect of Various Additives on Oxidation Resistance (Series I specimens)

Fig. 13 (a, b, c,) show the oxidation test results of the four specimens with boron bearing additives (DC 4 %, DS 4 %, DZ 4 %, DB 5 %) together with the specimen with alloy additive (DA 4 %) and the straight doloma–carbon specimen (DO) for comparison. The Fig. 13 (a) and (b) show the results of depth of oxidized layer and of weight changes respectively. The outward appearance of the cut sections of specimens after oxidation tests are shown in Fig. 13 (c). The values of the depth of oxidized layer and of weight changes after oxidation tests describe very similar tendencies.

It clearly demonstrates that the specimens with boron bearing additives exhibit much better oxidation resistance than the reference specimens (DA and DO) at all temperatures tested. In particular, the extent of oxidation at 1400°C and 1600°C for

specimens DC and DS is only 1/5 ~ 1/20 of DA and DO, indicating the dramatic effects of boron addition on inhibition of carbon oxidation. The order of merit in terms of oxidation resistance is DC > DS > DZ > DB < DA > DO, i.e. as antioxidant, CaB_6 > Bc > ZrB_2 > colemanite > alloy.

From Fig. 13 (a) and (b), another interesting feature of significant importance for the oxidation behavior of specimens with born bearing additives is that with temperature increase, (from 1200 °C to 1600 °C), the oxidation resistance is improved remarkably.

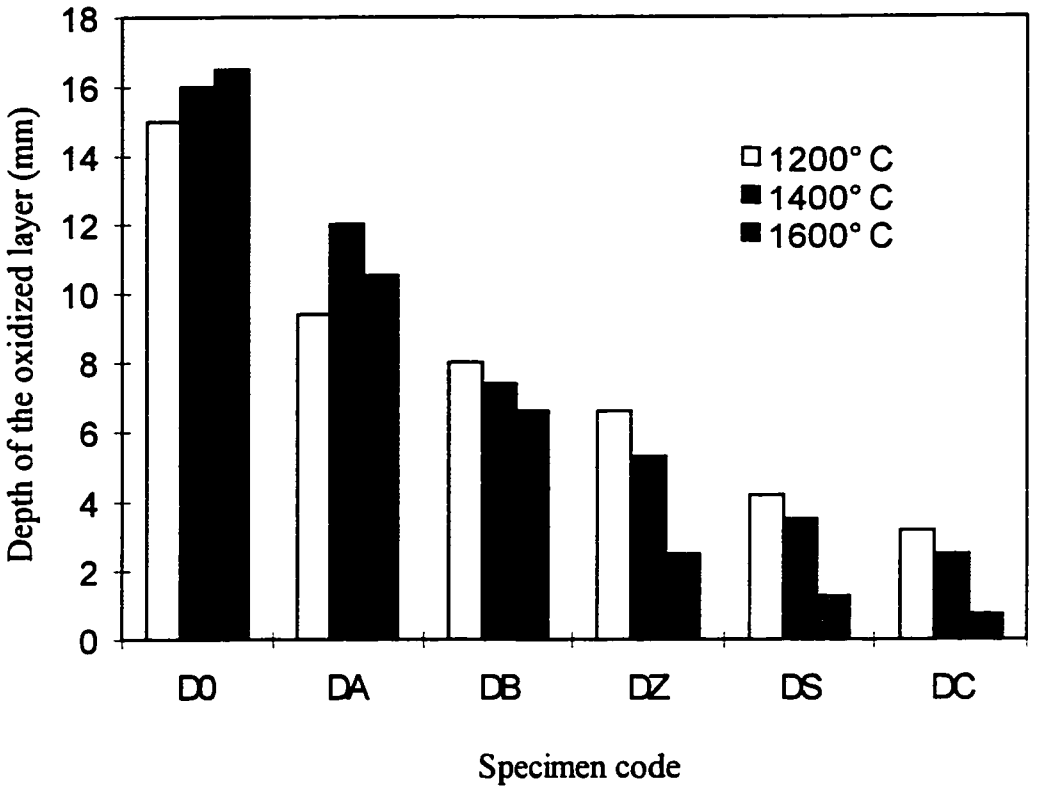


Fig.13 (a). Depth of oxidized layer after oxidation tests for series I specimens With 4 % addition for DA, DC, DS, DZ and 5 % for DB

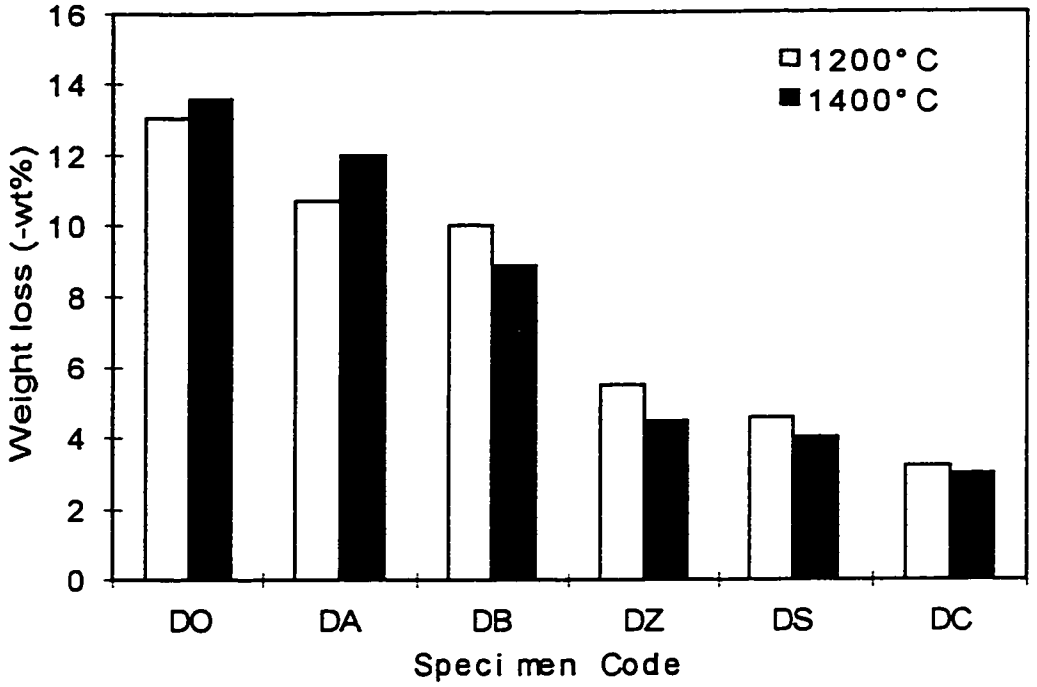


Fig.13 (b). Weight loss after oxidation tests for series I specimens

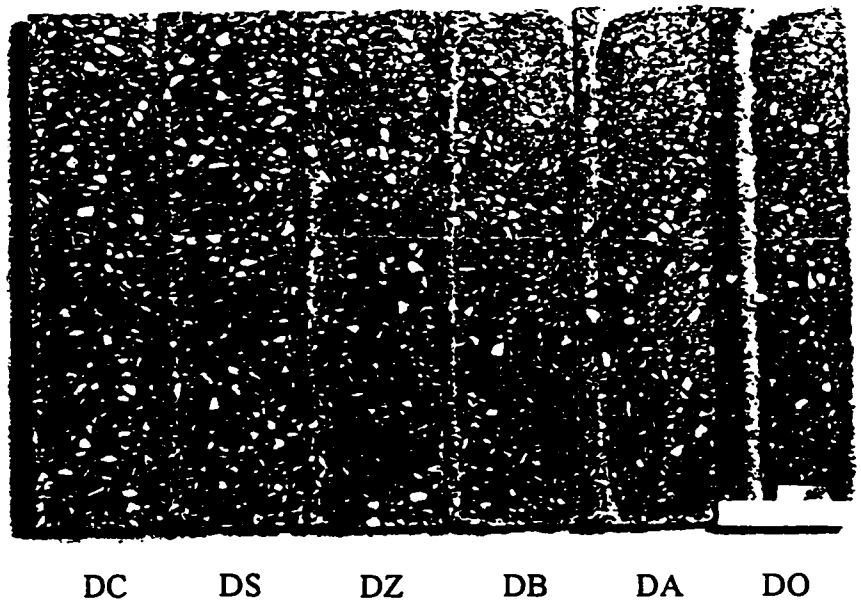


Fig.13 (c). The outward appearance of sectioned series I specimens after oxidation tests

5.1.2 Effect of Varying Amount of Additives on Oxidation Resistance (Series II specimens)

Fig. 14 (a) and (b) show the depth of the oxidized layer and weight changes of specimens after oxidation tests (1200°C and 1400°C) for specimens DC, DS and DZ with varying amount (from 2 to 4 %) of additives.

With an increase amount of additive, the extent of oxidation is decreased, but not drastically between 3% to 4% addition. The depth of the decarbonization layer and weight loss of the specimens after oxidation tests give concordant results. The specimens are more sensitive to oxidation at 1200 °C rather than at 1400°C.

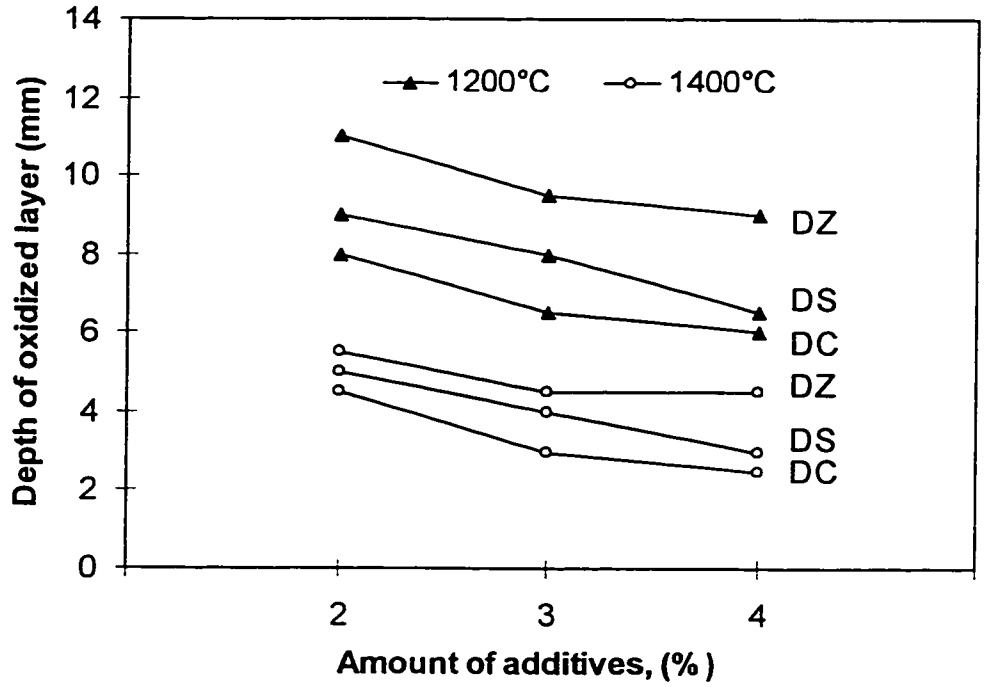


Fig. 14 (a). Variation of depth of oxidized layer after oxidation test with amount of additives for DC, DS, DZ specimens, as in series II

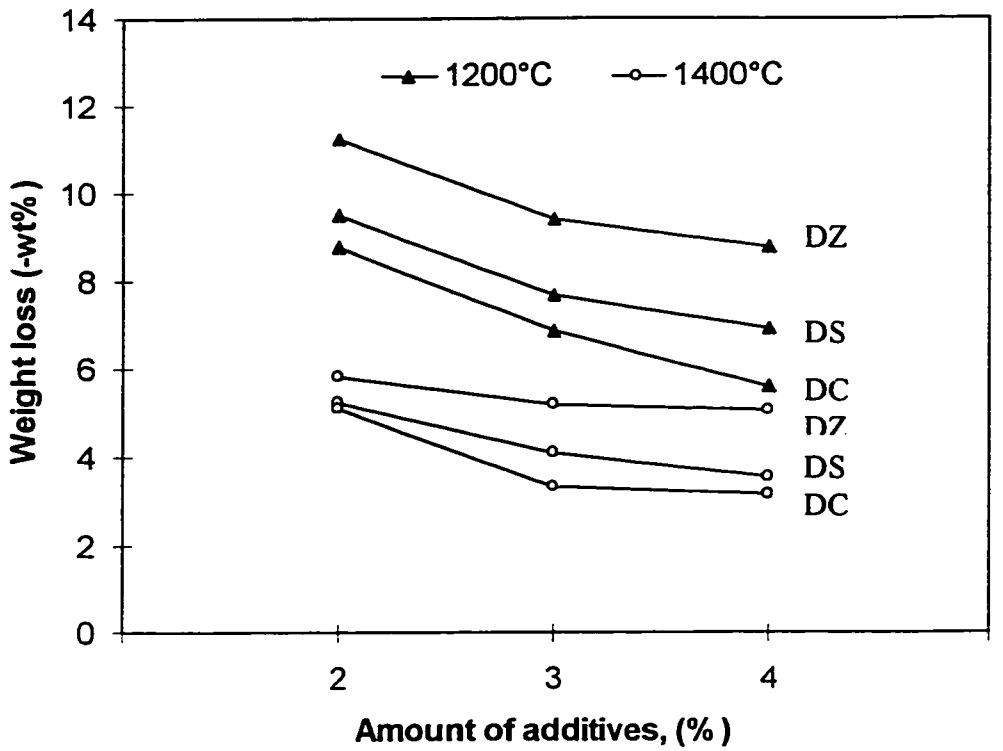


Fig. 14 (b). Weight losses after oxidation test, with various amount of additives for DC, DS, DZ specimens, at 1200 °C and 1400 °C

5.1.3 Effect of Mixed Additives on Oxidation Resistance (Series III specimens)

(A). Fixed Ratio (2 : 2) of Mixed Additives (CaB_6, ZrB_2, Bc and Mg–Al alloy)

Fig. 15 shows the effect of simultaneous addition of boron bearing materials (CaB_6, ZrB_2, Bc) and alloy, (DCA, DZA and DSA; mixed ratio = 2 : 2) on oxidation behavior as compared to boron bearing additive alone . The extent of oxidation is very close between mixed antioxidant and boron bearing antioxidant alone, (e.g. DCA vs DC, DSA vs DS, DZA vs DZ).

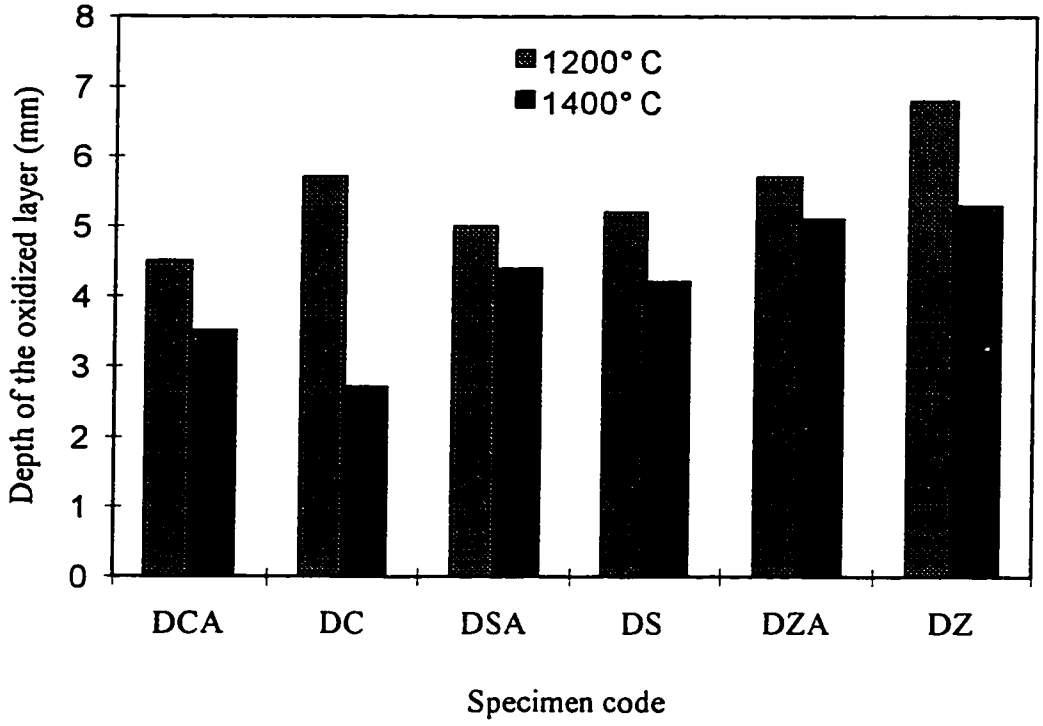


Fig. 15. Depth of oxidized layer after oxidation tests

(B). Varying Ratio of Mixed Additives (Bc and Mg-Al alloy)

Different oxidation results are obtained with varying Bc / alloy ratio.When the amount of boron bearing additives is fixed and amount of Mg-Al alloy addition is varied (DSA 1:2 vs DSA 1:3; DSA 0.5:2 vs DSA 0.5:3), the effect on oxidation resistance is insignificant (see Fig. 16-a). But, when the amount of boron bearing additives is varied and amount of Mg-Al alloy addition is fixed (DSA 2:2 and DSA 1:2 and DSA 0.5:2; DSA 1:3 vs DSA 0.5:3), greater difference in oxidation behavior is observed (see Fig. 16-b). The specimens with higher boron bearing addition have a better oxidation resistance, showing in that the contribution of boron bearing materials to oxidation resistance is greater than that of alloy.

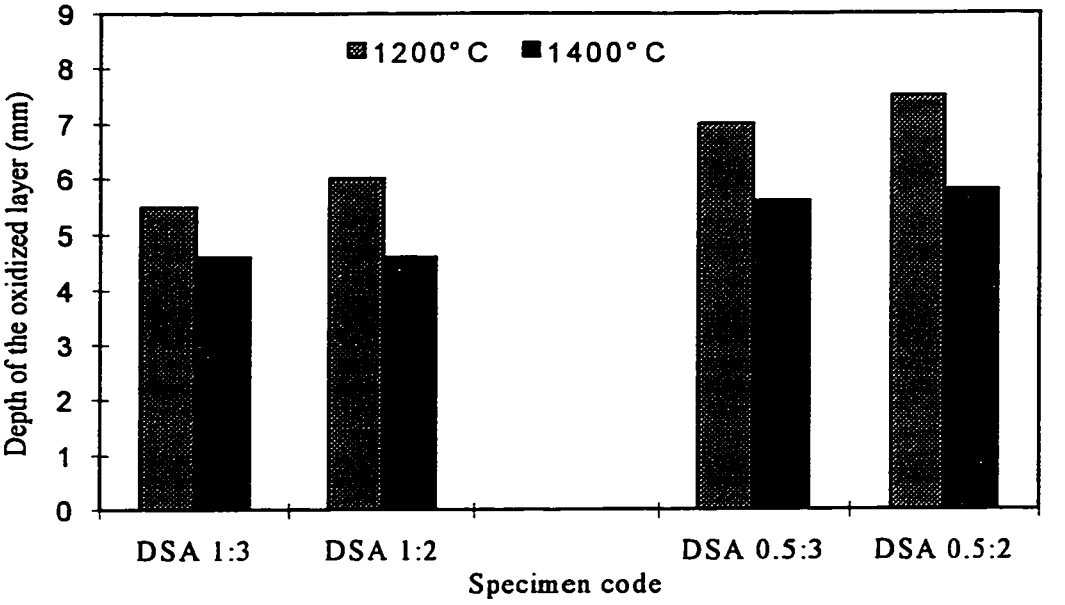


Fig 16 (a). Results of oxidation tests illustrating the effect of the ratio Bc to alloy, at two levels of Bc contents: 1 % and 0.5 %

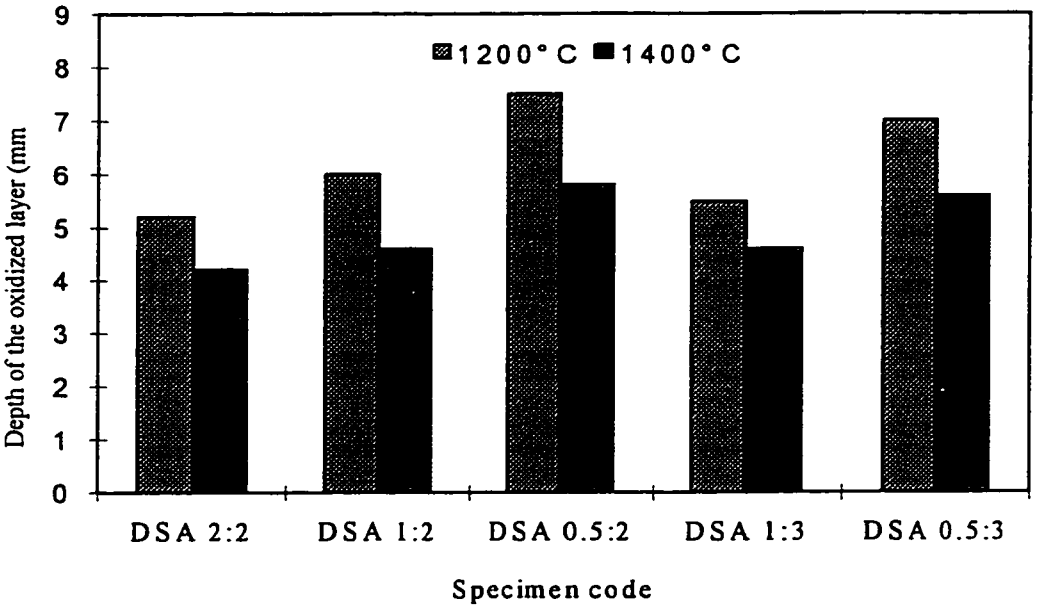


Fig 16 (b). Results of oxidation tests illustrating the effect of the ratio Bc to alloy, at two levels of alloy contents: 2 % and 3 %

5.2 Oxidation Tests on Magnesia-Doloma-Carbon Materials

The oxidation test results of the four magdoloma-carbon specimens with boron bearing additives (MDC, MDCA, MDS and MDZ) and two reference specimens MDA (with Mg-Al alloy additive) and MDO (without additive) are shown in Fig. 17 (a) and (b). It can be seen that the oxidation behavior of magdoloma-carbon specimens with boron bearing additives and mixed additives is much better than that of the reference specimens (MDA and MDO) at all temperatures tested. The depth of the oxidized layer at 1400°C and 1600°C for specimens MDC and MDCA is only 1/4 ~ 1/16 of reference specimens MDA and MDO. The oxidation behavior of these magdoloma-carbon specimens shows similar tendencies as corresponding doloma-carbon specimens. But at high temperatures (1400°C and 1600°C), their extent of oxidation is slightly greater than that of doloma-carbon specimens as shown in Table 10, indicating the effect of boron bearing additives on oxidation resistance of magdoloma-carbon specimens is less than of doloma-carbon specimens.

Table 10. The comparison of oxidation extent of specimens

Specimen code	Depth of the oxidized layer (mm)	
	1400 °C	1600 °C
DC	2.5	0.5
MDC	2.6	0.8
DS	3.5	1.2
MDS	3.6	3.1
DZ	5.2	2.5
MDZ	5.4	4.1

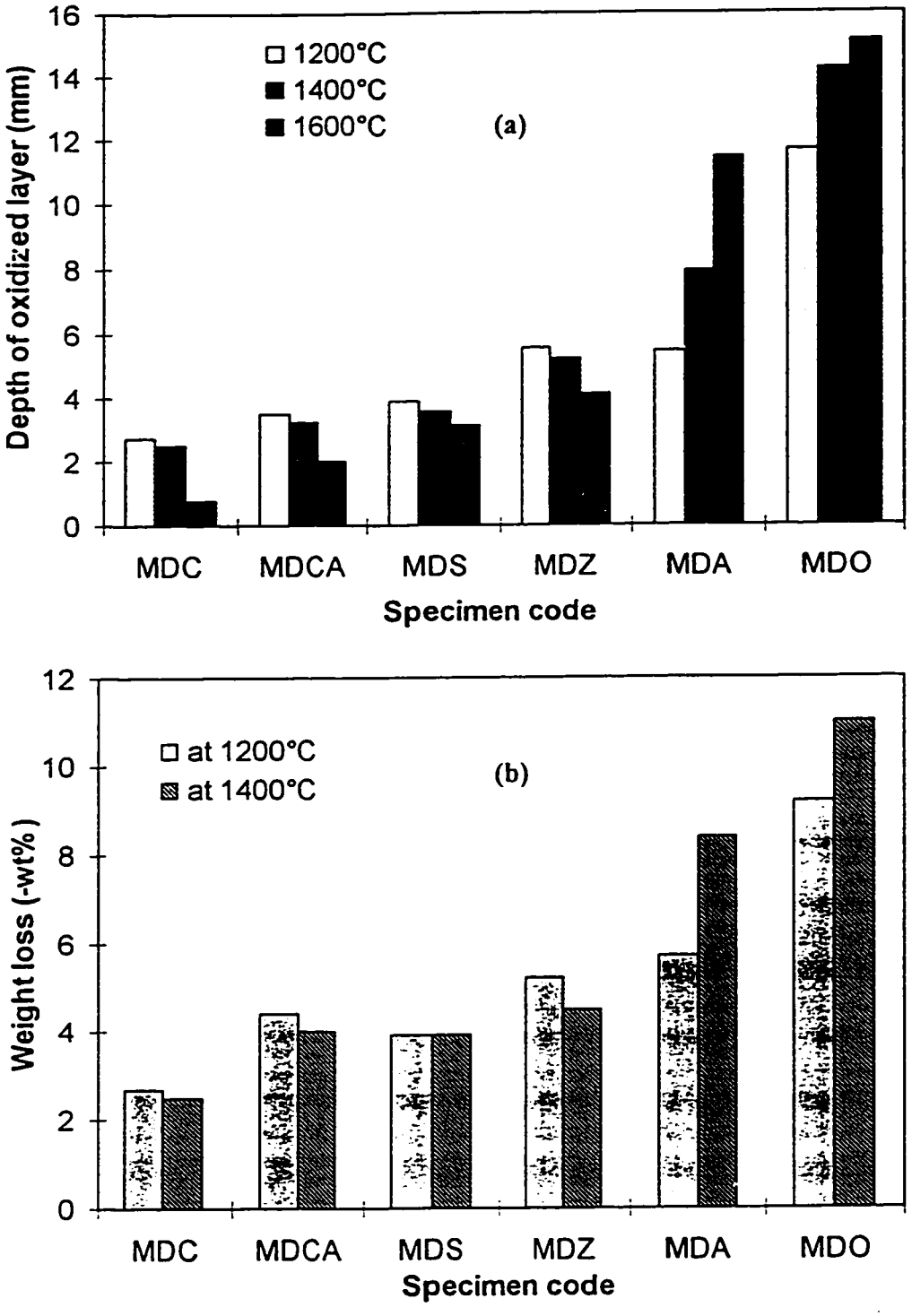


Fig. 17 Results of oxidation tests on magdoloma-carbon specimens with different antioxidants,(a) depth of oxidized layer; (b) weight loss

5.3 Phase Composition and Microstructure of the Oxidized Layer on Doloma and Magdoloma Specimens

After oxidation at 1400 °C and 1600°C, the formation of a glazing thin layer (due to a borate melt) on surface of the boron bearing specimens was observed. The results are a function of the boron content in the specimens, the higher it is (e.g. specimen DC), the thinner is the oxidized layer. Boron contents in the specimens are listed in Table 11.

Table 11. Boron content introduced to specimens

Specimen code	DC	DS	DZ	DCA	DSA	DZA
Boron content (%)	2.47	2.20	0.76	1.24.	1.10	0.38

5.3.1 XRD Analysis

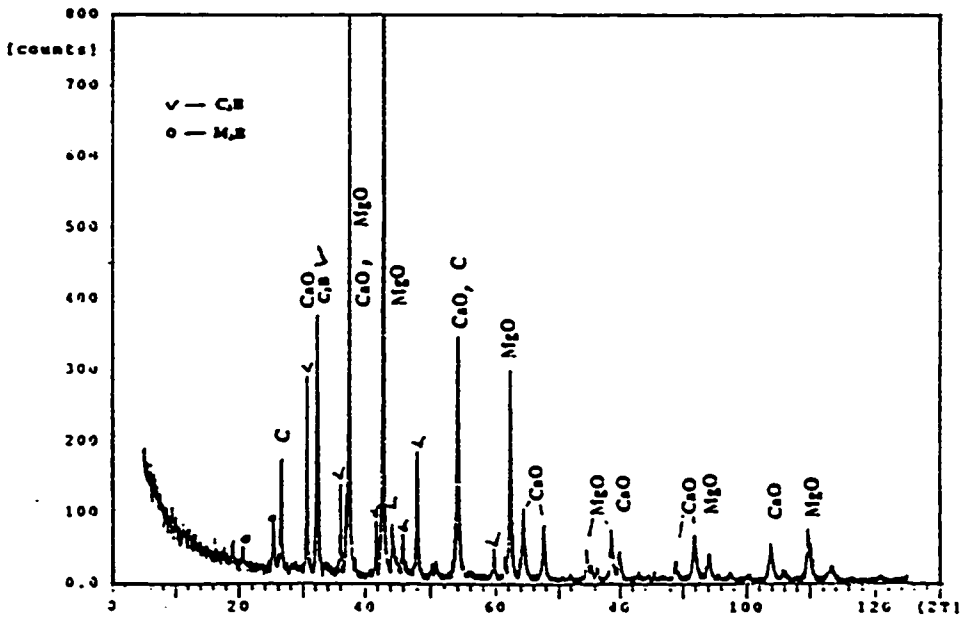
The results of XRD analysis on oxidized layer of four specimens with boron bearing additives and two specimens with mixed additives and one reference specimen DA (with Mg-Al alloy) indicate that the main crystalline phases are CaO and periclase and the newly formed borate minerals are mostly $Ca_3B_2O_6$ and some $Mg_3B_2O_6$. This is so not only in specimen DC with CaB_6 and DB with colemanite (see Fig. 18 a and b), but also in specimen DS with the Mg(B material Bc (see Fig. 18 c). This suggests that B_2O_3 preferentially reacts with CaO. For specimen DZ after oxidation, $Ca_3B_2O_6$ and $CaZrO_3$ are observed (see Fig. 18 d) . It is interesting to note that for specimen DA with

Al–Mg alloy addition, after oxidation, $Ca_3A_{l2}O_6$ is formed; there is no formation of $MgO{\cdot}A_2O_3$ as in the case of MgO–C materials. The results of XRD analysis on oxidized layer of specimens with mixed additives (boron bearing additives and Mg-Al alloy) indicate that new minerals formed are mainly $Ca_3B_2O_6$ and $Ca_3Al_2O_6$. The newly formed mineral phases by X-ray analysis on decarbonization layer of these specimens are summarized in Table 12.

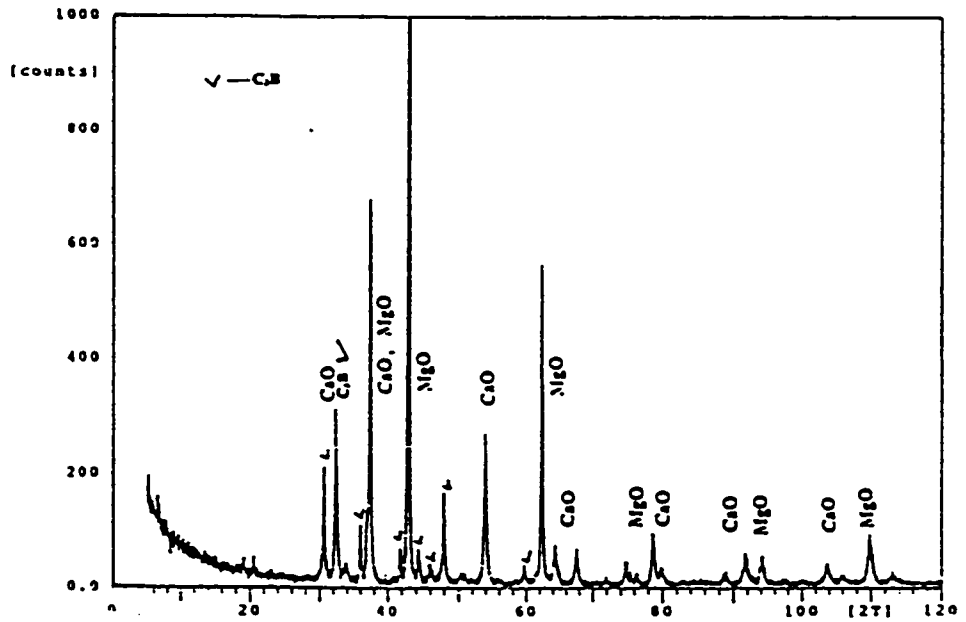
Table 12. Main new minerals detected by XRD analysis on oxidized layer

Specimen code	1200 °C × 3h	1400 °C × 3h	1600 °C × 3h
DC 4 %	C_3B	C_3B, C_3M*	C_3B, C_3M*
DS 4 %	C_3B	C_3B, C_3M*	C_3B, C_3M*
DZ 4 %	C_3B	C_3B, ,CZ*, C^3M*	C_3B, CZ, ZrO_2* C_3M*
DB 5 %	C_3B	C_3B, C_3M*	C_3B, C_3M*
DA 4 %	C_3A	C_3A	C_3A
MDC 4 %	C_3B	C_3B, C_3M*	C_3B, C_3M*
MDS 4 %	C_3B	C_3B, C_3M*	C_3B, C_3M*
MDZ 4 %	C_3B	C_3B, ,CZ*, C_3M*	C_3B, CZ, C_3M*

* very little amount

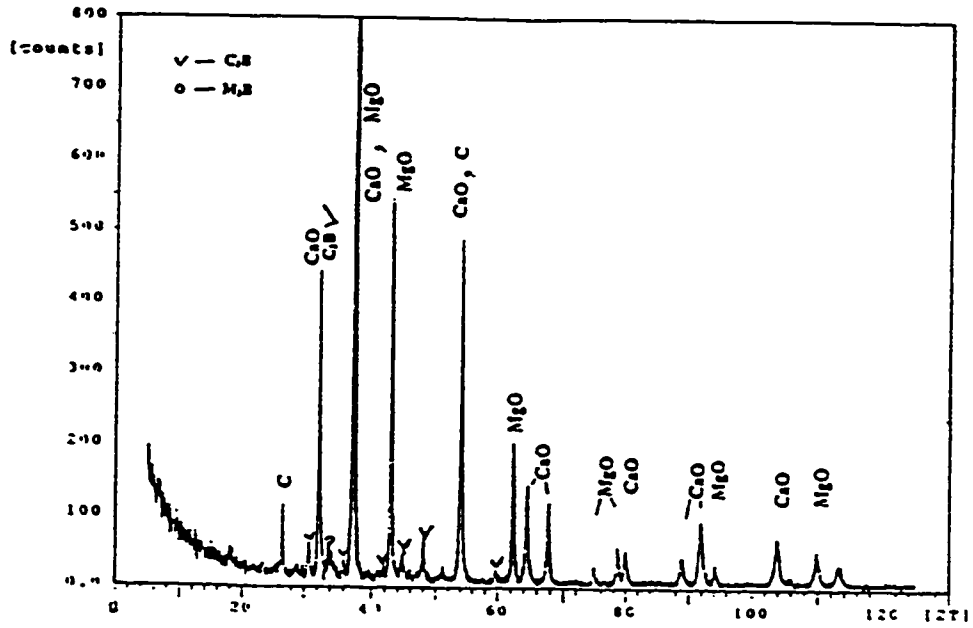


(a)

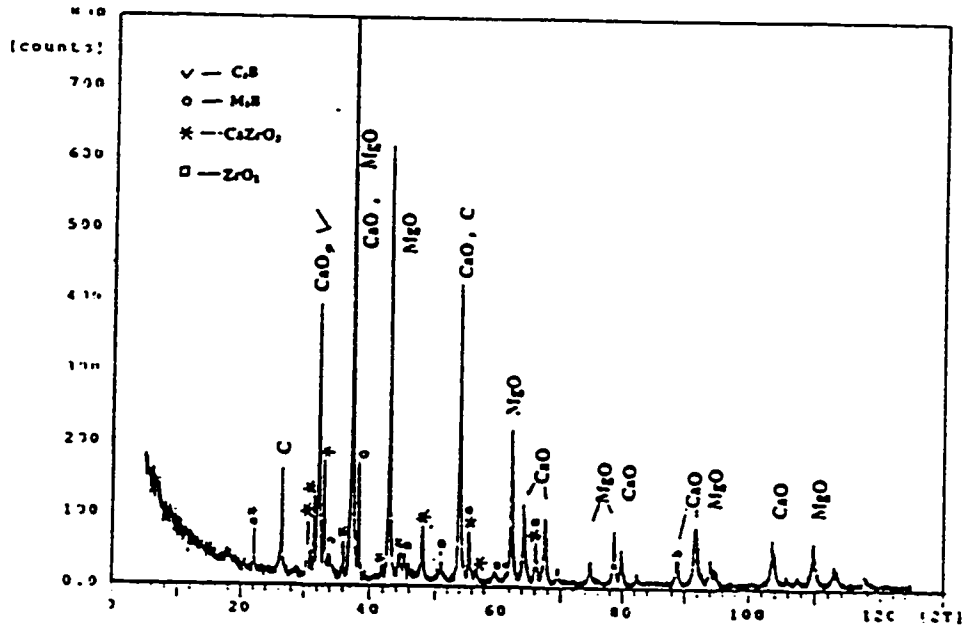


(b)

Fig. 18 a-b. Results of the XRD analysis of specimens DC(a) and DB(b)



(c)



(d)

Fig. 18 c--d. Results of the XRD analysis of specimens DS(c) and DZ(d)

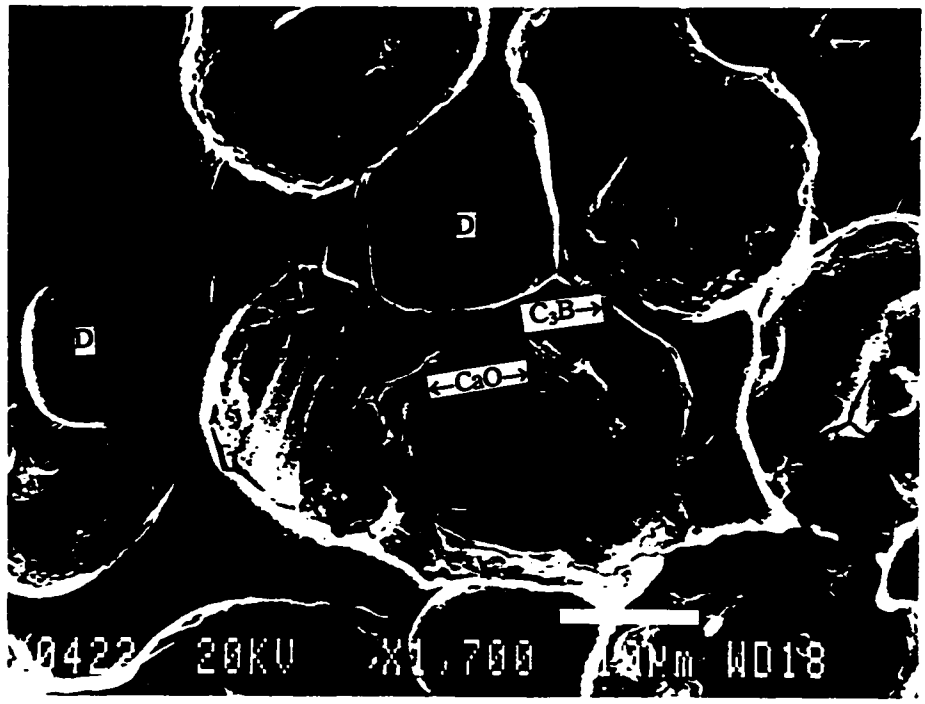
5.3.2 SEM and EDX Examinations

SEM observations show that the microstructural characteristics of the oxidized layer of specimens with boron bearing additives are quite similar. Fig. 19-a (specimen DC) is a typical SEM photo of oxidized layer of these series of specimens. The skeleton structure is composed of CaO and MgO crystals as expected. The borate (predominantly $Ca_3B_2O_6$) as bridge(like long thin crystals link the main crystals to form continuous network structure.

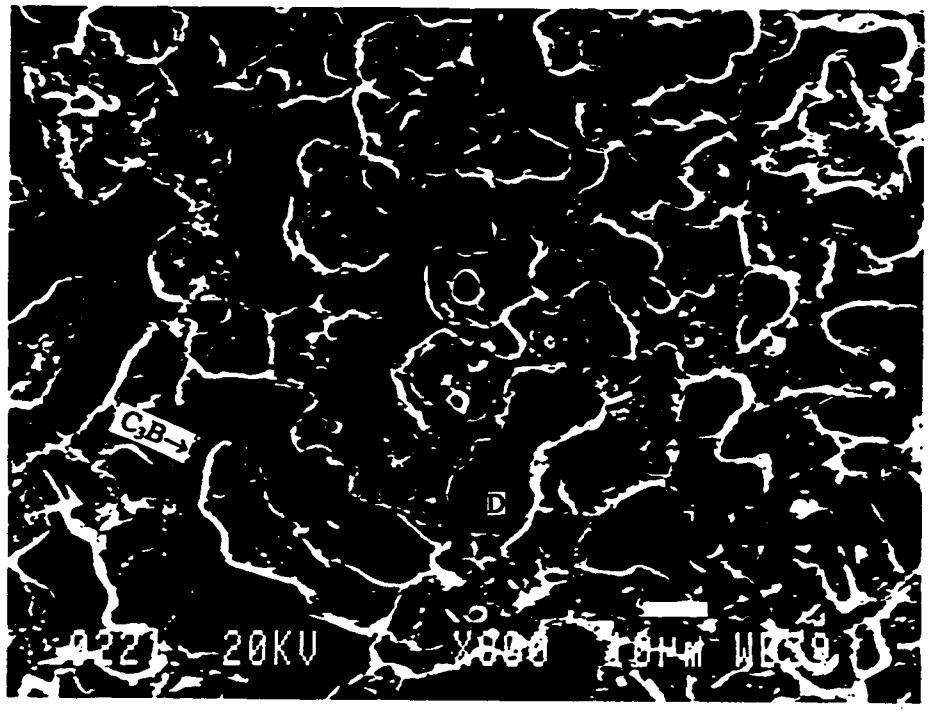
In the case of specimen DZ where the borate content is lower, the network structure is intermittent (see Fig. 19- b).

Besides, another characteristic of oxidation resistance of boron bearing specimens is that there is no transition layer between oxidized layer and unchanged area. This is different from the case of carbon containing materials in general where there is a transition zone with gradual decarbonization.

It may be inferred that the product of boron oxidation, B_2O_3 , reacts with CaO and MgO to form mostly $Ca_3B_2O_6$ and some $Mg_3B_2O_6$. The borate melt upon cooling crystallizes out as bridge-shaped structure linking the main crystals (CaO and MgO).



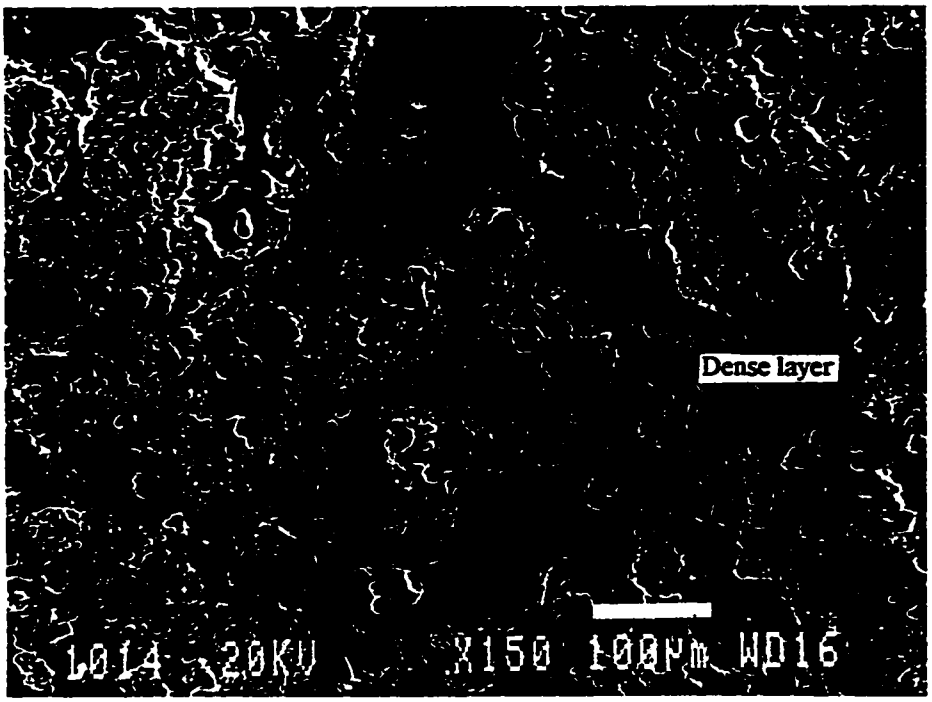
(a). DC



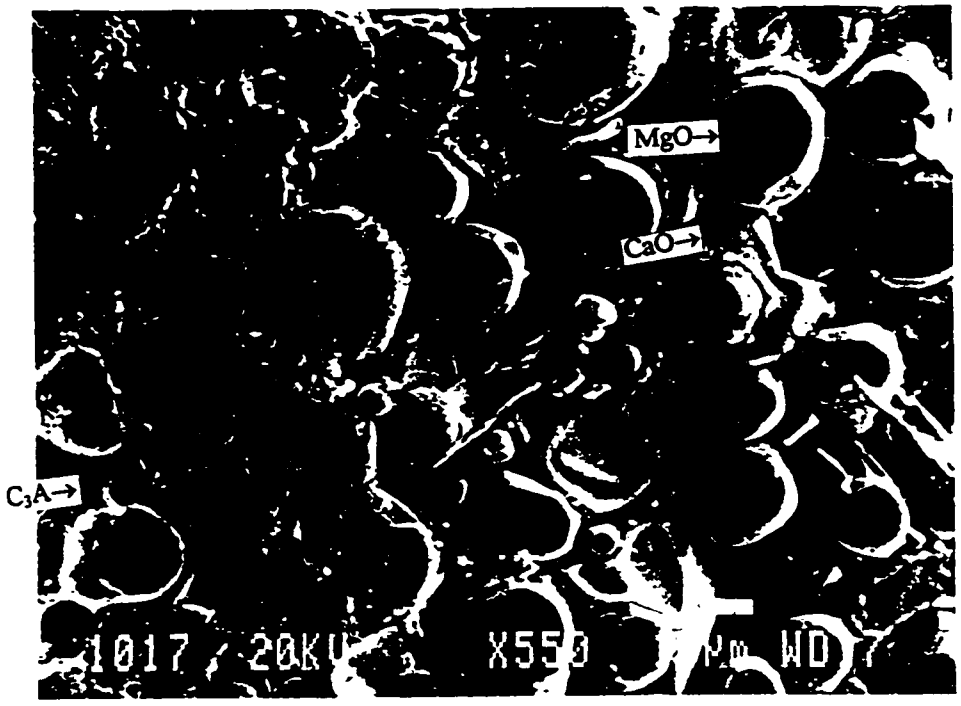
(b). DZ

Fig. 19 SEM photos of the oxidized layer of specimens (a) DC, (b)DZ

Fig 20-a is SEM photograph of specimen DA (with Mg-Al alloy additive) after oxidation test at 1600°C. It shows that between the unchanged zone and oxidized layer, there is a transition layer where carbon content is gradually reduced from inside to outside. Al is oxidized to Al_2O_3 which reacts with CaO to form $Ca_3Al_2O_6$. In the oxidized layer, the material is gradually sintered from inner face to outer face due to the action of $Ca_3Al_2O_6$. At the outer surface, a dense layer is formed, which would reduce the contact between oxygen and carbon. On the dense surface of this layer, very small MgO crystal are observed as shown in Fig 20-b.



(c).



(d)

Fig. 20 SEM photos of the oxidized layer of specimens DA

5.4 Interpretation of Results

It is well known that boron and metallic boride can easily be oxidized to B_2O_3 at lower temperature than carbon, and B_2O_3 reacts with CaO and MgO to form calcium borate and magnesium borate:

$$3CaO + B_2O_3 \rightarrow Ca_3B_2O_6 \qquad (5\text{--}1)$$

$$3MgO + B_2O_3 \rightarrow Mg_3B_2O_6 \qquad (5\text{--}2)$$

It is also well known that CaO is more reactive than MgO and in basic refractories, the impurity oxides (SiO_2, Al_2O_3, Fe_2O_3, B_2O_3) would preferentially react with CaO. Therefore in doloma(carbon material, with boron bearing additives (alone and mixed) as antioxidant, the oxidation product is predominantly Ca3B2O6 , as revealed in our test results reported above.

According to T. R. Lipinski [6,7,36] and Hayashi [55] et al, some $Mg_2B_2O_5$ is formed between 700°C ~ 800°C, but it decomposes at 1000°C ~ 1200°C and the B_2O_3 liberated reacts with CaO to give $Ca_3B_2O_6$, i.e:

$$2\,MgO + B_2O_3 \rightarrow Mg_2B_2O_5 \qquad (\text{at } 700°C \sim 800°C) \qquad (5\text{--}3)$$

$$Mg_2B_2O_5 \rightarrow 2\,MgO_{(s)} + B_2O_{3(g)} \qquad (5\text{--}4)$$

$$B_2O_{3(g)} + CaO \rightarrow Ca_3B_2O_6 \qquad (\text{at } 1000°C \sim 1200°C) \qquad (5\text{--}5)$$

Hayashi et al [55] have reported that in the $CaO–B_2O_3$ system, the evaporation of B_2O_3 is inhibited. D.J.Griffin et al [56] in their study on oxidation resistance of doloma-carbon refractories have reported that since the MgO in the dolomite materials is surrounded by CaO, it is not as intimately associated with the carbon and, therefore not

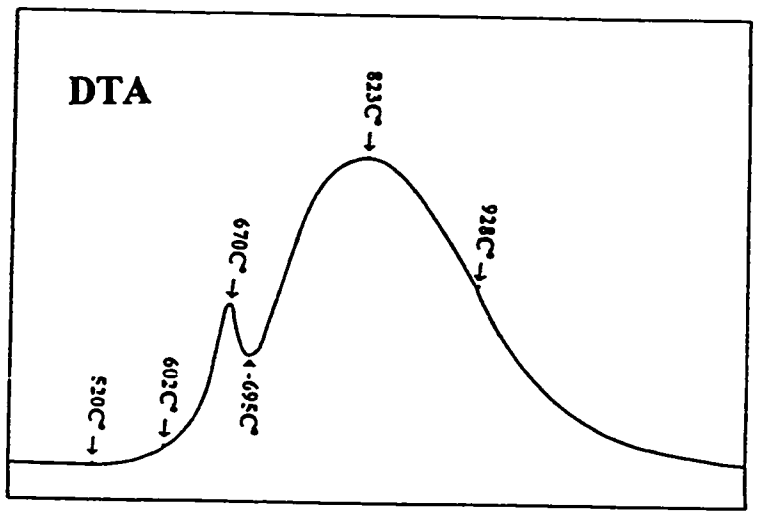
as readily reduced. Hence a dense MgO zone would appear to take longer time to form, and so MgO has less effect on oxidation resistance. These may help to explain why even in specimen DS with Mg-B additive, the final oxidation product is also predominantly $Ca_3B_2O_6$, (see Fig. 18-- c).

In all the oxidation tests, another characteristic, of significant importance for the oxidation behavior of specimens with boron bearing additives is that with temperature increase (from 1200°C to 1600°C), oxidation resistance is improved noticeably as indicated by the significant reduction in depth of oxidized layer after oxidation tests shown in above Fig. 13 ~ 17.

Rigaud and his co-workers [8,9,43] have postulated the contribution of borate melt to the improvement of oxidation resistance of carbon bonded basic refractories with Bc and B_4C additions. From conventional phase diagrams [57], It can be seen that the eutectic temperatures of $Ca3B_2O_6$–CaO, $Mg_3B_2O_6$–MgO, MgO–$Ca_3B_2O_6$–$Mg_3B_2O_6$ systems are 1460°C, 1330°C and 1080°C respectively. In our series I specimens, the matrix of the oxidized layer is composed of $Ca_3B_2O_6$, $Mg_3B_2O_6$, CaO and MgO, most probably with minor amount of silicate. It may be deduced that at 1200°C, borate melt formation has begun and contributed to retardation of carbon oxidation. With increase of temperature to 1400°C and 1600°C, the amount of borate melt increases accompanied by simultaneous lowering of viscosity, thus forming a liquid phase protective layer which would considerably reduce contacts between oxygen and carbon. This explains the

phenomenon that for all specimens with boron bearing additives, oxidation resistance is noticeably increased with temperature rise.

The oxidation behavior of ZrB_2 examined by DTA and TGA is shown in Fig. 21 (a) and (b).



(a)

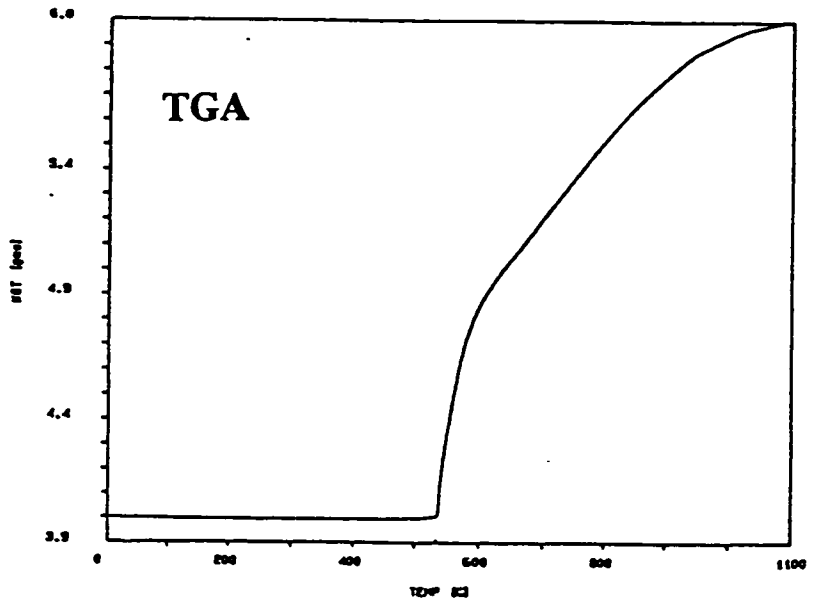


Fig. 21 DTA and TGA of ZrB_2

In the DTA curve, three exothermic peaks are observed at 550°C, 670°C and 823°C. In the TGA curve, a gain in weight due to oxidation of ZrB_2 begins from about 540 °C and continuously increase with steady rate up to 1100°C, at this temperature, total weight gain is 50 %.

ZrB_2 is easily oxidized to form ZrO_2 and B_2O_3, as such:

$$ZrB_{2(s)} + 5/2\ O_{2(g)} \rightarrow ZrO_2 + B_2O_{3(l)} \qquad (5\text{--}6)$$

In CO atmosphere, ZrB_2 reduces $CO_{(g)}$ to C according to the following reaction and thus decreases the oxidation of carbon:

$$ZrB_{2(s)}\ 5CO \rightarrow ZrO_{2(s)} + B_2O_3{}^{(l)} + 5C_{(s)} \qquad (5\text{--}7)$$

B_2O_3 will preferentially react with CaO to form calcium borate and ZrO_2 reacts with CaO to form $CaZrO_3$ with high melting point (2345°C).

In the case of metal addition, the Al_2O_3 formed reacts with CaO to form $Ca_3Al_2O_6$ which would partially fill in the interstices between grains. In CaO-MgO-C refractories, the effect of metal additive on oxidation resistance is not as significant as that of boron bearing additives, but wih mixed additives (metal additive and boron bearing materials), the effect of oxidation resistance is better because of the synergetic effect of two types of additives.

The effects of antioxidants (boron bearing materials and metal additives) on oxidation behavior of doloma(carbon and magdoloma-carbon materials may be considered to take place in the following two stages:

First, the boron or boride would react with oxygen, before carbon, to form B_2O_3. Likewise, Al or Al-Mg alloy would react with oxygen to form oxides or with carbon to form carbides. In this way, net oxidation of carbon is retarded. Second, the B_2O_3 reacts with CaO and MgO to form borate melt (liquid phase) protective layer on specimen surface at high temperature (1200 °C ~ 1600 °C which effectively protect carbon. The higher the temperature, the better is the anti-oxidation effect.

5.5 Conclusions of This Chapter

1). For doloma-carbon and magdoloma-carbon materials, boron bearing additives exhibit much better oxidation resistance at 1200 °C to 1600 °C than metallic additives. The extent of oxidation at 1400 °C and 1600 °C for specimens with boron bearing additives is only 1/5 ~ 1/20 that of reference specimen with metallic additive.

2). In the boron bearing additives used in this work, the order of merit as antioxidants for CaO–MgO–C materials is CaB_6 > Bc > ZrB_2 > colemanite > alloy. Optimum addition amount of boron bearing additives is 3 ~ 4 %.

3). Oxidation resistance of boron bearing specimens is improved noticeably with temperature increase (from 1200 °C to 1600 °C).

4). Mixed additives (boron bearing and Mg-Al alloy or Al powder) are also very effective as antioxidant due to synergetic effects of the two types of additives. The extent of oxidation tends to decrease with higher ratio of boron bearing additives to metallic additive.

5). The marked effect of boron bearing additives on oxidation resistance may be explained follows:

In the specimens with boron bearing additives, during oxidation, B_2O_3 reacts with CaO and MgO to form $Ca_3B_2O_6$ and $Mg_3B_2O_6$, predominantly the former which would form a borate melt protective layer to retard carbon oxidation.

CHAPTER 6. SLAG CORROSION RESISTANCE OF DOLOMA-C AND MAGDOLOMA-C REFRACTORIES

Seven doloma-carbon and magdoloma-carbon specimens with boron bearing additives are selected for the slag corrosion tests (DC, DCA, DSA, DZA and MD-CA, MD-SA, MD-ZA) together with two reference specimens without additive (DO, MDO) and one reference specimen with Mg-Al alloy alone (MDA).

Three steelmaking slags are used — EAF slag (grain size of < 6mm) for rotary test method; secondary refining slag and BOF slag (grain size of < 1mm) for crucible test method . Their chemical composition and basicity are shown in Table 13.

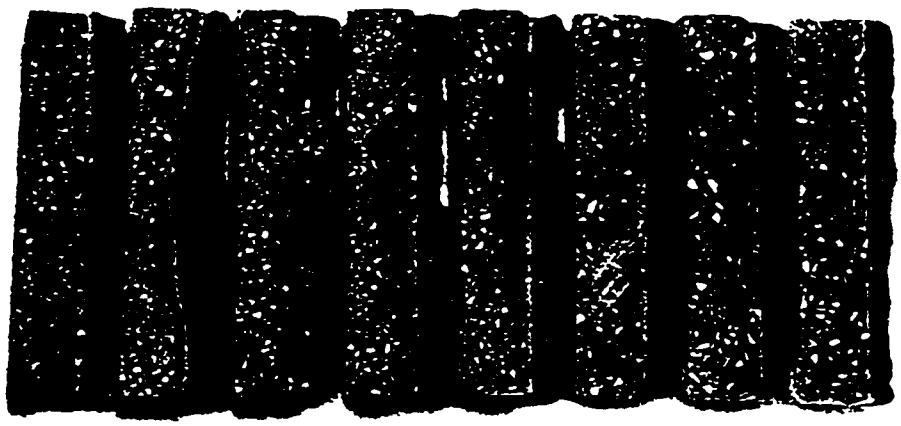
Table 13. Chemical composition and basicity of steelmaking slags

slag no.	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	MnO	P_2O_5	C / S
1	36.40	16.50	4.96	29.2	12.2	0.65	1.51	0.34	2.21
2	46.26	24.89	12.12	2.74	10.36				1.9
3	49.52	11.85	2.24	23.26	10.66				4.18

6.1 Slag Corrosion Tests by Rotary Method

Fig. 22 shows the outward appearance of the cut sections of the specimens after rotary slag test using EAF slag. Specimens DO and DC have been corroded much more

than the other specimens. By visual observation, all the residual specimens after corrosion test may be divided into three zones — slag zone, reaction zone and unchanged zone. The cross section of specimen DO shows loose structure. Its reaction zone is relatively thick (~ 4 mm), but that of specimens DC is thin about 0.5 mm, the same as for the other specimens with mixed additives.

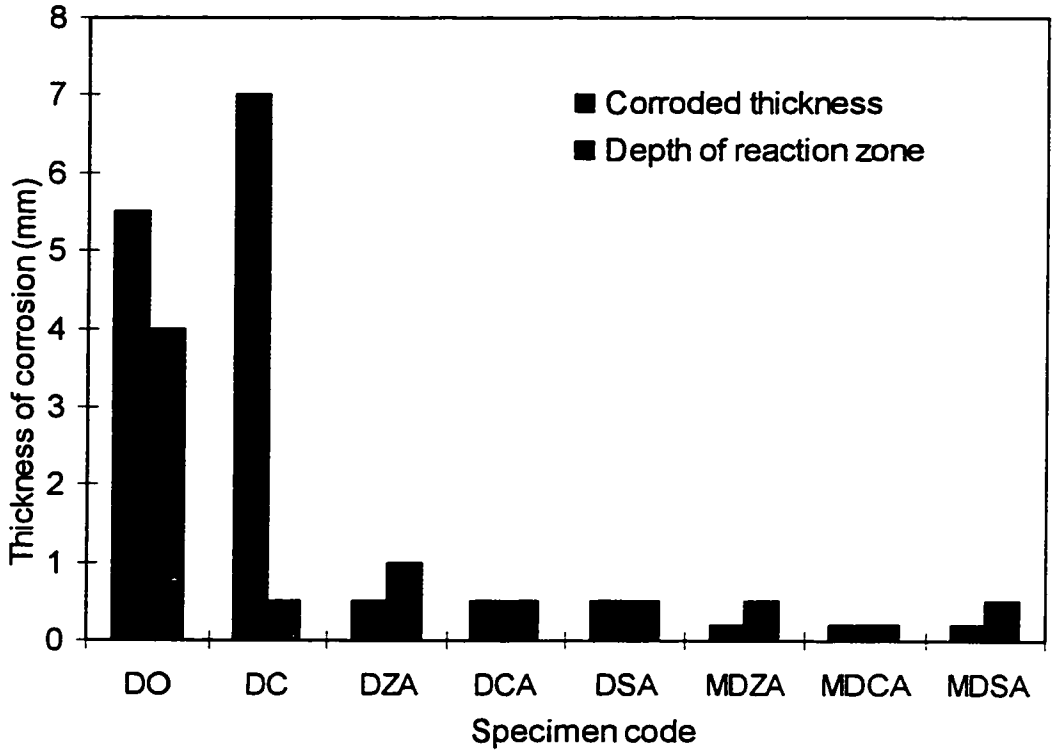


DO DC DCA DSA DZA MDCA MDSA MDZA

Fig. 22 Outward appearance of sectioned specimens after slag corrosion test

Two measurements are made for evaluation of corrosion behavior: (1) corroded thickness: initial thickness before test minus residual thickness after test; (2) depth of penetration: thickness of reaction zone in residual specimen. The former may serve as the criterion for evaluating extent of corrosion whereas the latter for estimating the extent of slag penetration.

Fig. 23 Shows the corroded thickness and depth of reaction zone of the specimens tested.



(* additive content: DO 0 %; DC 4 %; others 2 : 2)

Fig. 23 Corroded thickness and depth of penetration after slag test

From these figures, it can be seen:

(1). For doloma-carbon specimens, the corrosion resistance of specimen DC is lower than specimen DO, but that of specimens DCA, DSA and DZA is many times better than specimen DO. The corroded thickness of the latter three specimens is less than 0.5 mm, whereas that of specimen DO is 5.5 mm, that of specimen DC is 7 mm. In other words, with the introduction of boron bearing additive (CaB_6) alone, corrosion resistance is appreciably decreased due to relatively large amount of borate melt. But the simultaneous addition of boron bearing material (CaB_6, Bc or ZrB_2) and alloy (Al–Mg)

to doloma–carbon leads to dramatic improvement of slag resistance.

(2). Similarly, the magdoloma-carbon specimens with mixed additives (MDCA, MDSA and MDZA) exhibit improved corrosion resistance.

(3). In all boron bearing specimens investigated (DC, DCA, DSA, DZA and MDZA, MDSA, MDCA), depth of reaction zone is much less than that of specimen DO. The thickness of their reaction zone is all less than 1mm irrespective of the extent of corroded thickness; this is considerably less than that of specimen DO (4 mm). That is to say, the borate melt layer formed from oxidation of boron bearing additives after being oxidized would act as a barrier to protect carbon from oxidation and also to impede slag penetration.

6.2 Slag Corrosion Tests by Crucible Method

Fig. 24 and 25 show the results of the slag corrosion test with low basicity secondary refining slag (C/S = 1.9) and with high basicity BOF slag (C/S = 4.18) on doloma-carbon and magdoloma-carbon specimen crucibles with boron bearing additives and reference specimens (DO and MDO). By visual observation, all the residual specimens after corrosion tests may be divided into three zones slag zone, reaction zone and unchanged zone. At specimen — slag — gas interface, corrosion is greater. The cut sections of reference specimen (DO and MDO) show loose structure and they have been corroded much more than boron bearing specimens.

It is observed that in residual specimens after corrosion tests with high basicity BOF slag, residual slag is left in crucible hole. Analysis of the residual slag in crucible after

testing indicate that it is mainly composed of CaO, MgO and SiO_2 (total amount >95 %), and its principal mineralogical constituents are periclase and C_2S with high melting point. This indicates that at high temperature, low melting point and low viscosity minerals in the slag penetrate into the specimens and high melting point minerals are left behind.

It should be pointed out that the test results of specimen DC with 4 % CaB_6 by crucible method are different from those by rotary method, the corroded thickness is much greater for the later, but, thickness of the reaction zone is practically the same, this is because in the static crucible tests, the slag does not flow and there is no erosive action as in the case of dynamic rotary tests.

For specimen DO, after corrosion test with low basicity slag, when the crucible is taken out from the furnace and cooled, dusting occurs in the crucible hole. This dusting phenomenon is due to C_2S inversion from β to γ form at about 520°C. But, all other specimens with boron bearing additives do not show the dusting phenomenon. In order to inhibit this dusting phenomenon, one of the most successful ways is that a little amount addition of B_2O_3 added to CaO-containing materials can effectively prevent the $\beta \rightarrow \gamma$ change[58,59]. This effect is another contribution of boron bearing additives on improvement of corrosion resistance of doloma-carbon refractories, using low basicity slag .

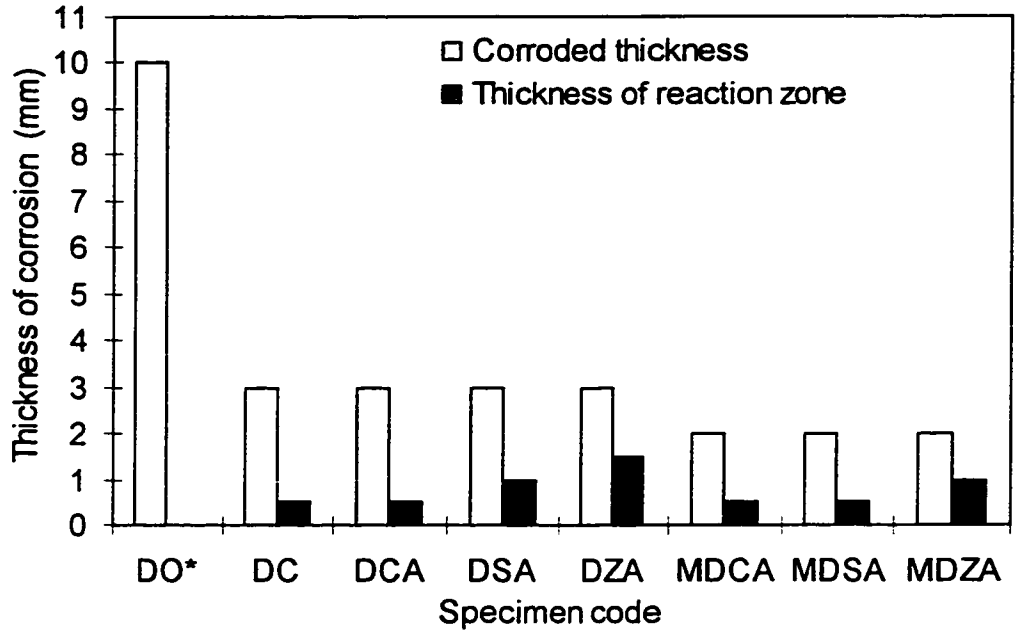


Fig. 24. Results of slag corrosion test with crucible method (slag C/S = 1.9)

* The corroded thickness include reaction zone thickness because of dusting of reaction zone.

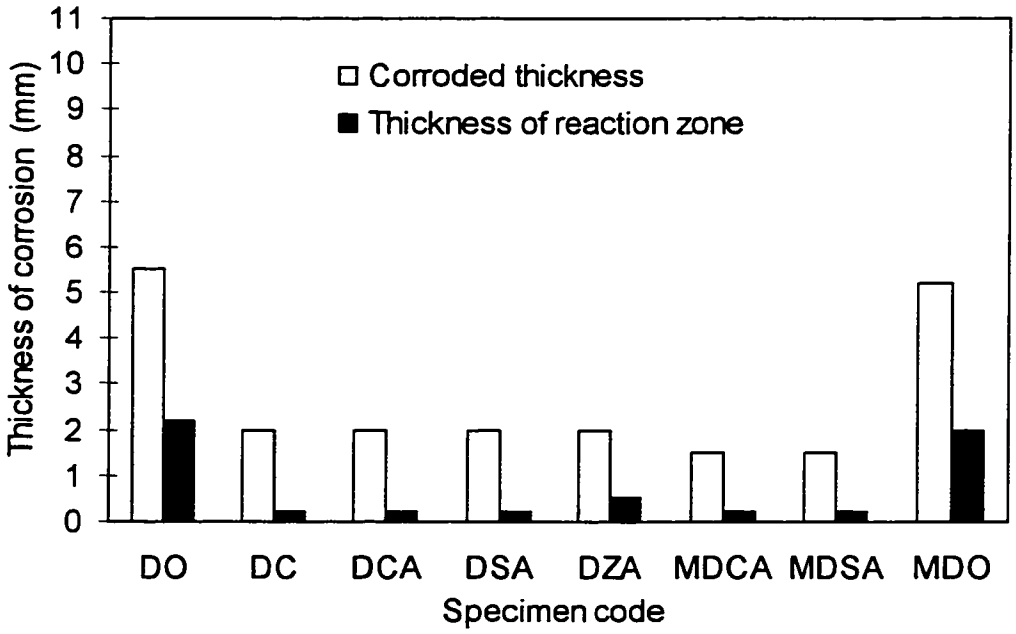


Fig 25. Results of slag corrosion test with crucible method (slag C/S = 4.18)

From the above results, it appears that :

1). Corrosion thicknesses of the specimens with different boron bearing additives are very similar. Such a result has to be put in perspective with the inherent limitation associated with such a test.

2). The specimens with boron bearing additives (alone and mixed) have better corrosion resistance than reference specimens. (Same remark applies; also, dusting after test seems the main contributing factor for such a difference).

3). For specimens with mixed additives, corrosion resistance of magdoloma-carbon specimens seems better than that of doloma-carbon specimens, but the difference is not truly significant.

4). Extent of corrosion by high basicity slag (C/S = 4.18) is appreciable less than that by low basicity slag (C/S = 1.9) as shown in Table 14.

Table 14. Corrosion results of doloma-C and magdoloma-C specimens by different basicity slags

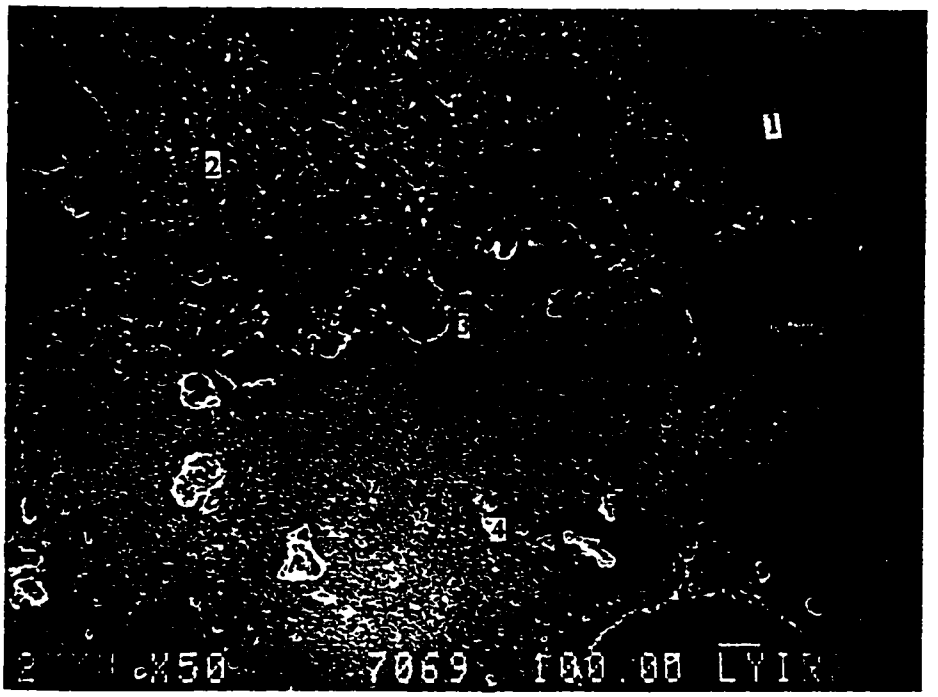
Specimen code	Corroded thickness (mm)	
	C/S = 1.9	C/S = 4.18
DCA	3.0	2.0
DSA	3.0	2.0
DZA	3.0	2.0
MDCA	2.0	1.5
MDSA	2.0	1.5

6.3 Microstructure of Specimens after Slag Corrosion Test

6.3.1. Microstructure of Specimens after Rotary Slag Tests

Fig. 26 is the photomicrograph of specimen DCA showing the three zones — unchanged zone, reaction zone and slag zone, after corrosion by slag CaO / SiO2 = 2.21.

Fig. 27 (a) and (b) are SEM photos of the reaction zone and unchanged zone of specimen DCA. From Fig. 27-a, it can be seen that the skeleton structure of CaO and periclase bridged by $Ca_3B_2O_6$ is quite similar to that in the case of oxidized layer after oxidation test, but the CaO and MgO crystals appear to be more rounded at the periphery and calcium ferrite is observed in the mass.



1. Dolomite grains, 2. Matrix (containing carbon),
3. Reaction zone, 4. Slag layer

Fig.26 SEM photomicrograph of residual specimen DCA showing the three zones

Fig. 27 (a). SEM photos of reaction zone of specimen DCA

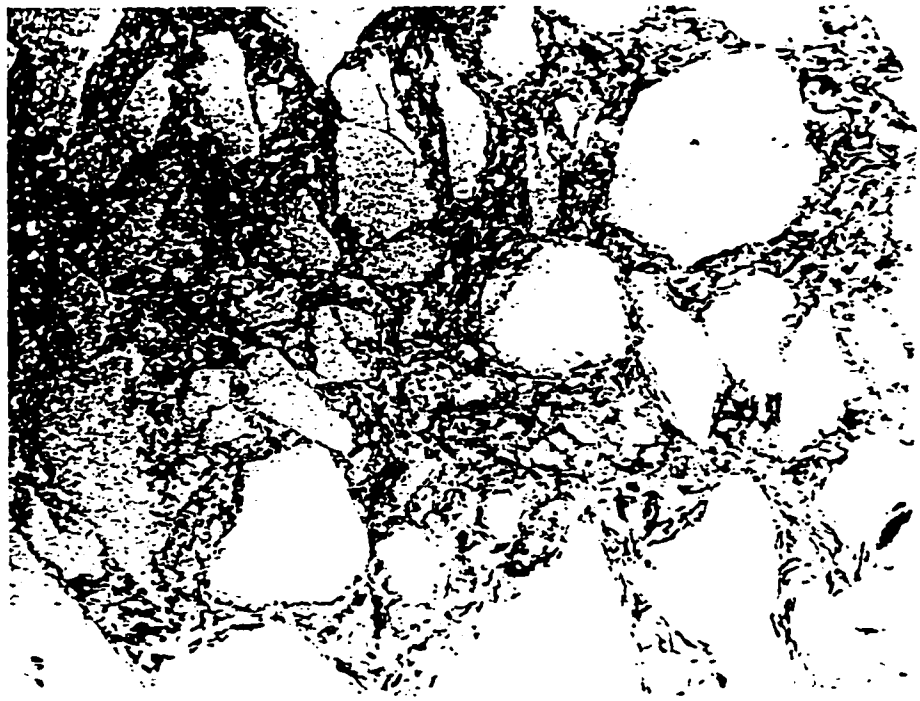


Fig. 27 (b). SEM photos of unchanged zone of specimen DCA

6.3.2. Microstructure of Specimens after Crucible Slag Tests (BOF slag, C/S = 4.18)

By SEM observation, the microstructure of unchanged zone of the boron bearing specimens is the same as that after rotary tests (see above Fig. 27- b). The reaction zone of all specimens with boron bearing additives (alone and mixed) is very thin and there is no transition zone. Fig. 28-a shows the three zones — slag zone; reaction zone and unchanged zone of specimen MDCA.

1. Slag zone; 2. Reaction zone; 3. Unchanged zone

Fig. 28 (a). photomicrograph of specimen MDCA corroded with crucible method

Fig. 28—b is SEM photo of the reaction zone (near slag zone) of specimen MDCA corroded by BOF slag. It can be seen that calcium ferrite is observed around periclase crystals in the mass and calcium silicate are also observed.

1. Periclase; 2. Calcium ferrite; 3. CaO (Hydrated)

Fig 28 (b). SEM photo of reaction zone of specimen MDCA

Fig. 28-c is SEM photo of slag zone of the specimen MDCA, from which periclase crystals are observed near the surface; the slag preferentially reacts with CaO in refractories to form calcium silicate and ferrite and some periclase crystals are left behind.

Fig. 28-c SEM photo of slag zone in crucible specimen MDCA

6.4 Interpretation of the Results

The wear of refractories by molten slag can be divided into two main classes: change of structure due to slag penetration and chemical dissolution or corrosion. For resistance to chemical corrosion, the usual measures are improvement of refractoriness and adjustment of slag composition. For prevention of slag penetration, the usual measures are reduction of porosity of refractories and increase of slag viscosity. In general, molten slag may enter into refractory body through various ways, such as: capillary channels (cracks and pores), grain boundaries and micropores. Slag intrusion due to diffusion through crystal lattice may be neglected because the diffusion rate is

very slow. Slag intrusion through liquid phase channels may also be neglected because the amount of liquid phase formed is very low for high purity materials. Therefore, we only have to consider the other two factors via capillary channels (pores) and grain boundaries. For a given materials, the depth penetration of molten slag into refractory can be expressed by J. J. Bilkerman's equation[60]:

$$X = \sqrt{\frac{r\,\sigma\,\cos\,\theta}{2\,\eta}\tau} \qquad (6\text{—}1)$$

Where: r is a radius of capillary channel

σ is a surface tension

θ is a dihedral angle

η is a viscosity of melt

τ is a time

In limited time τ, liquid volume of penetration into refractories through area S is:

$$V = S \cdot X = S\sqrt{\frac{r\,\sigma\,\cos\,\theta}{2\,\eta}\tau} \qquad (6\text{—}2)$$

For a given slag with fixed viscosity (η) and surface tension (σ), the two parameters to be consider in the above equation are capillary radius (r) (pore size and amount) and dihedral angle (θ). To reduce penetration of slag, pore size and amount should be decreased and dihedral angle should be increased.

The non-wettability of carbon by molten slag is well known; its dihedral angle with molten slag is greater than 90°. Thus, the carbon in refractories can obstruct penetration of liquid slag. Hence according to our work, protection of carbon in

refractories from oxidation through introduction of boron bearing additives would be beneficial.

The borate melt formed due to boron bearing addition (described in Chapter 5) would seal open pores of the refractories which effectively obstruct slag penetration. This may explain why, for all boron bearing specimens tested, irrespective of the ultimate extent of corrosion, the reaction zone of the residual specimens after slag tests is very thin (< 1mm), indicating very low slag penetration.

For carbon containing refractories, it has been postulated that slag attack on carbon bearing basic refractories may be considered to proceed in two stages. Carbon is first oxidized . After decarbonization, the principal action is chemical corrosion by slag[61,62]. Our investigations have shown that addition of boron bearing materials to doloma–carbon and magdoloma-carbon specimens would lead to pronounced increase in oxidation resistance due to the effect of borate melt. In the process of slag attack, slower oxidation of carbon would be beneficial and the formation of borate melt layer in decarbonized zone would impede slag penetration as well, resulting in very thin reaction layer in residual specimens. However, after decarbonization the chemical corrosion of the slag comes into important play. For specimen DC with 4 % CaB_6 and DCA with 2 % CaB_6 and 2 % alloy, the difference in the amount of borate melt explains why the matrix in the reaction zone is corroded more in DC rather than DCA. In the case of the specimens with mixed additives (boride and alloy) the amount of borate melt is less and high melting $Ca_3Al_2O_6$ is formed from oxidation of the alloy; the two effects contribute to the decrease in the rate of slag corrosion, at this stage. It may be summarized that in

the process of slag corrosion, at the first stage of decarbonization, both boron bearing and alloy additives have beneficial effects, the boron material being more effective. But in the second stage of chemical corrosion, boron bearing addition is detrimental and alloy addition is beneficial. Therefore, it is important to control the boron content. An optimized combination of the two types of additives would be appropriate.

6.5 Conclusions of This Chapter

1. The slag corrosion resistance of the doloma-carbon specimen DC with boron bearing additives alone (CaB_6) is found to be noticeably lower than reference specimen DO (without addition) by dynamic rotary test method. Since the dynamic test is more simulative of practical applications, It may be more appropriate to conclude that boron bearing additives alone is detrimental to corrosion resistance.

2. Doloma-carbon and magdoloma-carbon specimens with mixed additives (boron bearing additives and Mg-Al alloy) do exhibit much improved slag corrosion resistance as compared with reference specimens DO and MDO, of course, in within the limits imposed by both test methods: dynamic and static. Their corroded thickness is only 1/3 ~ 1/5 that of specimens DO and MDO; their penetration zone is all very thin (< 1mm) much lower than specimens DO and MDO (2 ~ 4 mm). This improvement is considered to be due to a synergetic effect between the two additives.

3. When chemical corrosion comes into play, the borate melt formation is detrimental to corrosion resistance. As indicated in the rotary test, the latter effect is greater.

CHAPTER 7: HOT MODULUS OF RUPTURE OF DOLOMA–CARBON AND MAGDOLOMA–CARBON REFRACTORIES

For the study of the effects of boron bearing additives on modulus of rupture at elevated temperatures, two sets of magdoloma-carbon specimens with boron bearing additives (8 specimens in all) have been investigated by means of conventional three point bending testing under controlled reducing atmosphere as this described in Chapter 4. Two reference specimens, one without additive and the other with Al powder addition only are tested together. The variation of MOR with temperature has also been studied for three selected specimens (DO, DCA and MDCA).

7.1 Hot Modulus of Rupture (HMOR) Tests

It is important to recall that all of the following tests have been carried out under reducing conditions, as described in Chapter 4.

7.1.1 Magdoloma-Carbon Specimens with CaB_6 Additive, Alone and Mixed with Al Powder

This set of specimens includes: (1). one specimen with 4 % CaB_6 additive (MDC); (2). five specimens with mixed additives of varying ratio (MDCA2—6); (3). two reference specimens (MDO and MDA).

Fig. 29 shows the HMOR results of these specimens, from which it can be seen that:

(1). The HMOR of all the specimens with boron bearing additives tested is higher than that of specimen without additive (MDO), but, lower than that of specimen with Al powder additive alone (MDA)

(2). The HMOR of specimens with mixed additives is higher than that of CaB_6 additive alone (MDC). In other words, in terms of high temperature strength, the order of merit is: Al powder additive > mixed additives > CaB_6 additive alone > without additive.

(3). The MDC specimen possesses slightly higher HMOR value than specimen MDO and the HMOR value of specimen (MD-CA1:3) is very close to that of MDA specimen (6.9 MPa vs 7.3 MPa). In specimen with mixed additives, with decrease of CaB_6 / Al ratio (i.e. increase of Al content), the hot strength at 1400 °C is increased.

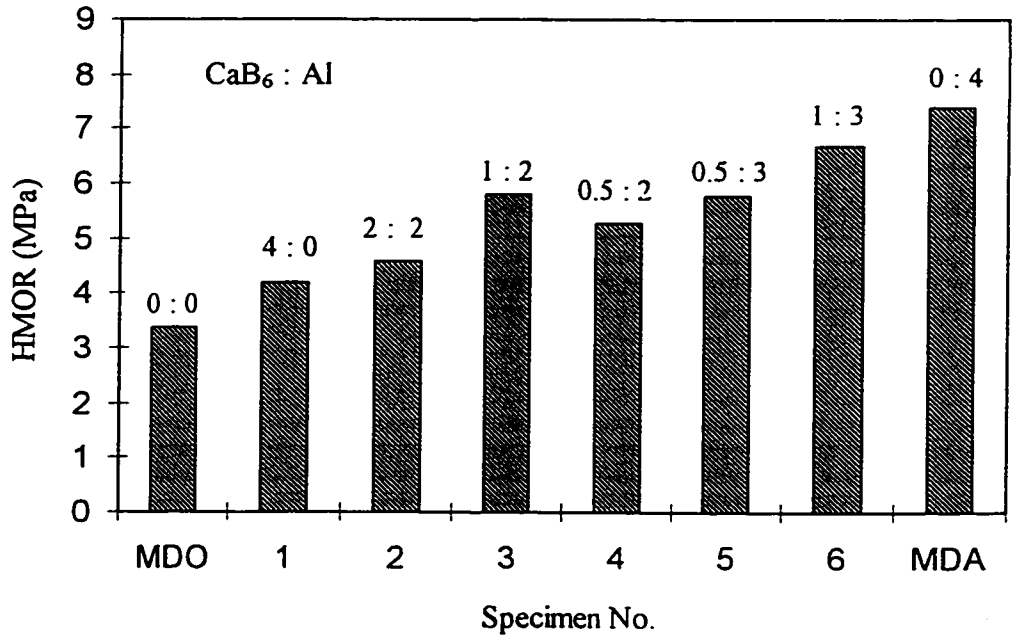


Fig. 29 Effect of varying CaB_6 / Al ratio on HMOR of magdoloma-C specimens at 1400°C

It may be concluded that the effect of Al powder additive on hot strength is more significant than that of boron bearing additives. Similarly, in the specimens with mixed additives, the contribution of Al powder additive to hot strength increase is greater. From the stand point of improved hot strength, the optimum ratio of CaB_6 and Al powder seems to be 1 : 3.

7.1.2 Specimens with Mixed Additives, Using CaB_6, Bc and ZrB_2 Additives and Al Powder

In this group, three specimens with mixed additives (boron bearing additives and Al powder) have been tested. The boron bearing additives used are CaB_6, Bc and ZrB_2. The ratio of the boron bearing additives and Al powder is 2 : 2. Their hot MOR results are shown in Fig. 30.

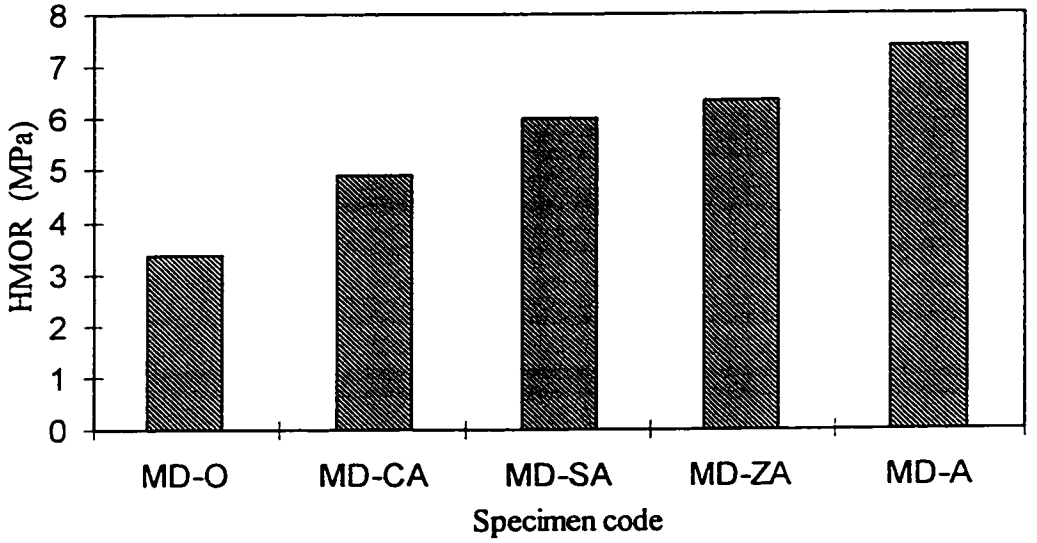


Fig. 30 Effect of the mixed additives on HMOR of the magdoloma-C specimens at 1400°C, (Boron compounds : Al = 2 : 2)

These HMOR results confirm the above viewpoint that the hot strength of specimens with mixed additives is superior to that of specimen without additive, but inferior to that of the specimen with Al powder additive alone. The HMOR values of specimen MDCA, MDSA and MDZA are very close (5 ~ 6.3 MPa), specimen MDZA being a little better.

7.1.3 Variation of MOR with Temperature

MOR — Temperature curves of three specimens (DO, D-CA_{13} and MD-CA_{13}), are shown in Fig. 31.

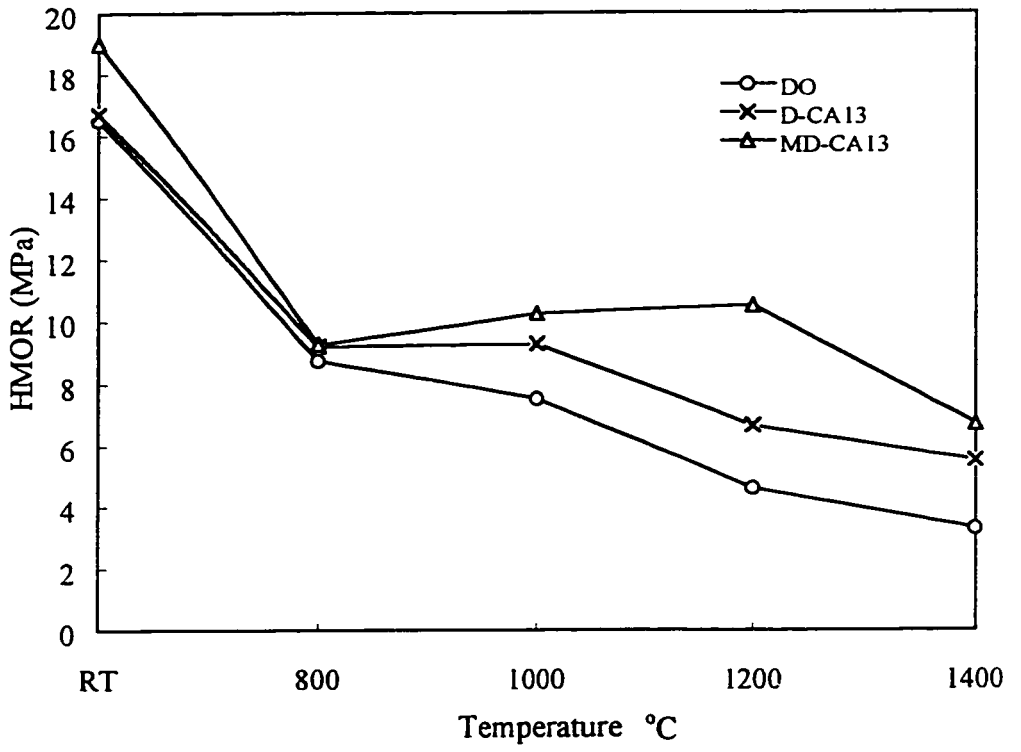


Fig. 31 HMOR — Temperature curves of doloma-C and magdoloma-C specimens

1). For all three specimens, the HMOR value at 800 °C (8.7 MPa) is noticeably lower than that at room temperature (16 ~ 19 MPa).

2). For specimen DO, the strength continuously decreases from 800°C to 1400°C. For specimen DCA, there is no changed in hot strength in the region of 800°C to 1000°C, after which the strength decreases up to 1400°C. For specimen MDCA, from 800°C to 1200°C, a slight increase in strength is observed; from 1200 °C to 1400°C, hot strength drops but remains the highest.

3). In terms of MOR value from 800°C to 1400°C, the order of merit is MDCA > DCA > DO, i.e. specimens with mixed additives are better than specimens without additive and magdoloma-carbon specimens are better than doloma-carbon specimens.

7.2 Phase Composition and Microstructure of Specimens after HMOR Tests

Phase composition and microstructure of specimens (MDCA, DCA) after the hot modulus of rupture tests (1400°C) under reducing atmosphere have been investigated by means of XRD and SEM analysis.

Fig. 32 shows the microstructure of specimens MDCA. It is composed of periclase and CaO as main crystal; graphite is present in the form of vein structure of continuous or semi-continuous nature as it is generally observed in carbon bonded basic refractories.

Interlocking needle shaped Al_4C_3 crystals are observed bridging the gaps between carbon and the oxide grains as shown in Fig. 33 (a) and (b).

Fig. 32 Photomicrograph showing graphite vein structure in matrix, in the MDCA specimen.

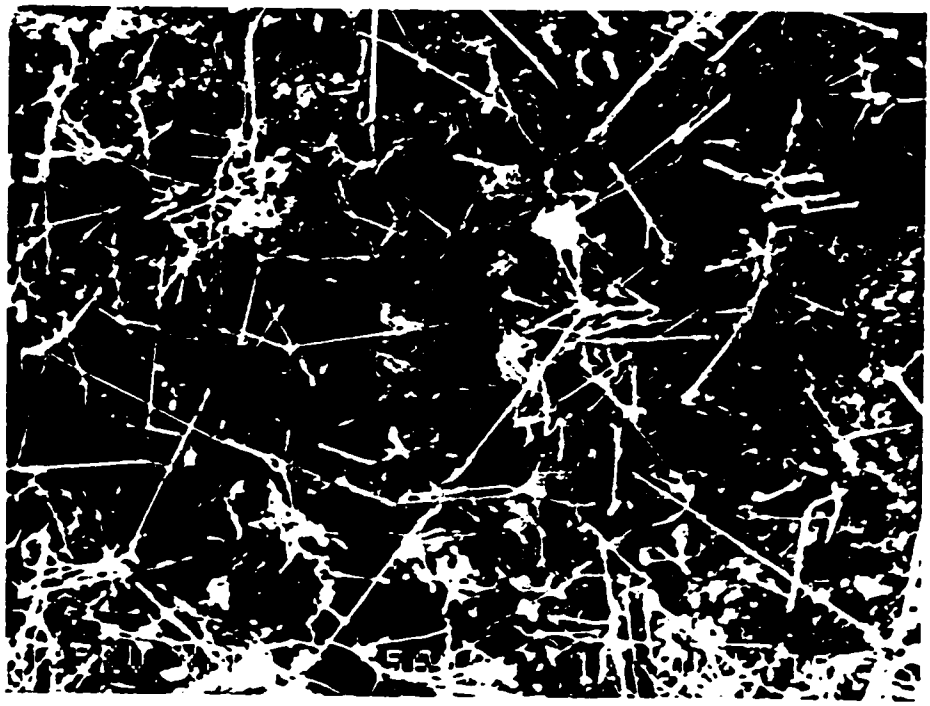


Fig. 33-a . Photomicrograph showing needle-shaped structure of Al_4C_3, which have been formed during the HMOR measurement.

Fig. 33-b. Photomicrograph showing needle-shaped Al_4C_3, under the same conditions, at higher magnification (X 2000)

XRD analysis also shows that Al_4C_3 is formed at 1000 °C to 1400 °C (see Fig. 34, XRD pattern). From the XRD and SEM examinations, no significant change in the CaB_6 is observed and also no symptom of oxidation or decomposition of the boride are found. This suggests that under controlled reducing conditions, the boride in specimens remains intact.

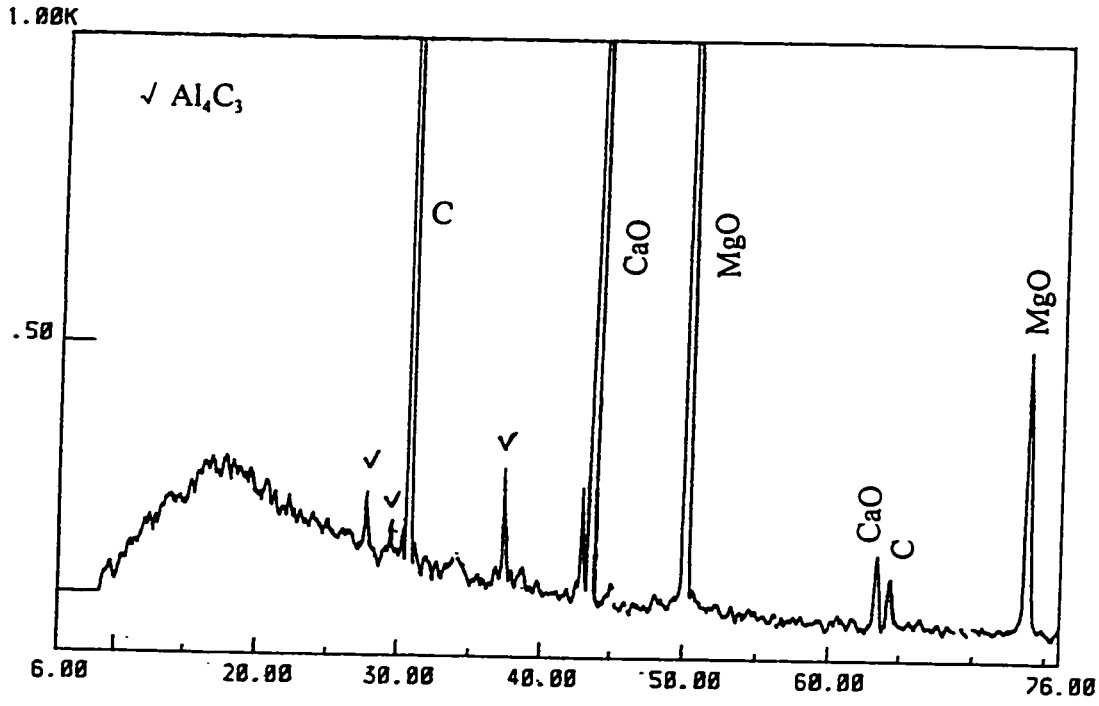


Fig. 34 XRD pattern of specimen D-CA_{13} after HMOR test

7.3 Interpretation

It is well known that the addition of metal powder (such as Al, Mg-Al alloy) to carbon bonded refractories do lead to noticeable improvement in strength properties at elevated temperatures[63,64,65]. The Al additive will react with carbon above 800°C to form Al_4C_3 which will bridge the gaps between carbon and oxide grains, creating a reinforcing effect. Our experimental results confirm the positive strengthening effect of Al additive.

An interesting results is that the magdoloma-carbon specimen with 4 % CaB_6 addition possesses the same or slightly higher level of HMOR value as the original magdoloma-carbon specimen without additive (HMOR: 4.2 MPa for MDC; 3.4 MPa for MDO). This indicate that under controlled reducing conditions, there is no formation of low melting borate and therefore, hot strength will not be lowered.

Our experimental results also indicate that the simultaneous addition of boron bearing additives (CaB_6, Bc and ZrB_2) and Al powder exert a synergetic effect on the strength properties at elevated temperatures. Based on our observation by XRD and SEM, there is no reaction whatever between boride and metal. The two additives play their roles separately. This explains that in the specimens with mixed additives, with increase of Al powder or decrease of CaB_6 / Al ratio, HMOR is increased and optimum CaB_6 / Al ratio is suggested to be 1 : 3. It may be concluded that the contribution of Al powder to hot strength is greater than that of boron bearing additives.

Another feature worthwhile noticing is that in terms of MOR values at elevated temperature (1000°C to 1400°C), specimen MDCA is better than DCA. It is reported[66,67] that strength of materials depends on: 1). properties of bond phases, 2). material structure, 3). strength of each component in the materials, and boundary correlation between these components. In our tests, since the type and amount of graphite, additives and bonding phase are similar and the process of specimen preparation and testing procedure are also similar, the difference in strength of specimen D-CA_{13} and MD-CA_{13} can only be attributed to the magdolmite clinker and dolomite clinker. The crystal lattice energy of periclase is greater than that of CaO, (MgO:

3935.59 kJ / mole; CaO: 3571.34 KJ / mole)[68]. Because magdoloma is richer in MgO, more energy is needed to rupture this material, its strength is expected to be higher than doloma material.

CHAPTER 8: COMPREHENSIVE DISCUSSIONS AND SUGGESTIONS

The effects of boron bearing additives on oxidation resistance, slag corrosion resistance , and hot strength of doloma-carbon and magdoloma-carbon materials have been systematically studied in this work. The specimens investigated include:

1. Three series of doloma-carbon specimens with boron bearing additives
   - A). Series I : with varying type of boron bearing additives (CaB_6 Bc, ZrB_2 and colemanite)
   - B). Series II : with varying amount (2, 3, 4 %) of CaB_6 Bc and ZrB_2 .
   - C). Series III: with mixed additives of boron bearing additives and Mg-Al alloy, including:
     - (a). With fixed ratio (2 : 2) of boron bearing additives and alloy
     - (b). With varying Bc / alloy ratio
2. Two sets of magdoloma-carbon specimens with boron bearing additives
   - A). With varying types of boron bearing additives (CaB_6 Bc and ZrB_2)
   - B). With varying CaB_6 / Al ratio
3. Four reference specimens — doloma–C and magdoloma–C specimens:
   - A). With metal additive alone
   - B). Without additive

All together 48 specimens have been tested.

For oxidation resistance tests, two methods have been used:

(1). In box furnace (1200°C and 1400°C)

(2). In rotary furnace (1600°C)

For slag corrosion resistance tests, two methods have been adopted:

(1). Rotary method (dynamic test)

(2). Crucible method (static test)

Three steelmaking slags have been used for corrosion tests. They are:

(1). EAF slag (C/S = 2.21)

(2). Secondary refining slag (C/S = 1.9)

(3). BOF slag (C/S = 4.18)

For HMOR tests, conventional three point bending method have been used, under reducing condition.

8.1 Oxidation Resistance

Oxidation tests on doloma-carbon and magdoloma-carbon specimens have indicated that:

(1). The specimens with boron bearing additives show better oxidation resistance than the reference specimens without additive and with metal additive alone at all temperatures tested, e.g. the extent of oxidation at 1400°C and 1600°C for specimen DC and DS is only 1/5 ~ 1/20 of DA and DO, that of MDC and MDCA is only 1/4 ~ 1/16 of MDA and MDO. The order of merit in terms of oxidation resistance is DC > DS >

DZ > DB > DA > DO, i.e. as antioxidant, CaB_6 > Bc > ZrB_2 > colemanite > alloy. The optimum amount of boron bearing additives for oxidation resistance is 3 ~ 4 %.

(2). The specimens with mixed additives of boron bearing additives and Mg-Al alloy have slightly lower oxidation resistance than specimen with boron bearing additives alone, but still much better than specimen DA (with metal additive). With increase of ratio of boron bearing additives and Mg-Al alloy, the oxidation resistance tends to increase; when ratio of boron bearing additives and alloy is 2 : 2, the oxidation resistance of specimen DCA, DSA and DZA is very close to that of specimen DC. It may be concluded that in the mixed additives, the contribution of boron bearing additives to oxidation resistance is much greater than that of metal addition.

(3). For all the boron bearing specimens, oxidation resistance increases with increase of temperature.

8.2 Corrosion Resistance

The results of the study on effects of boron bearing additives on slag corrosion resistance of doloma-carbon and magdoloma-carbon specimens have shown that:

(1). When tested by the dynamic rotary method, the slag corrosion resistance of doloma-carbon specimen with boron bearing additive (CaB_6) is noticeably lower than that of reference specimen DO (without additive); but, when tested by the static crucible method, it is better than the reference specimen DO. Since the dynamic test is more simulative to practical application, it should be deduced that boron bearing

additive alone is detrimental to corrosion resistance. In static crucible tests, because the molten slag does not flow, there is no erosive action on the crucible specimen sidewall, thus, the extent of corrosion is not as large as in dynamic test. However, it is interesting to notice that in both methods for all boron bearing specimens, the reaction zone is very thin (< 1mm), irrespective of corroded thickness, this indicates that slag penetration is impeded by the presence of boron compounds.

(2). All doloma-carbon and magdoloma-carbon specimens with mixed additives (ratio 2:2 of boron bearing additives and metal additive) tested exhibit much improved slag corrosion resistance as compared with reference specimens (without additive), both in the dynamic rotary tests and in the static crucible tests. The corroded thickness of specimens with mixed additives is only 1/3 ~ 1/5 that of specimen DO and MDO.

(3). For specimens with mixed additives, the extent of corrosion by high basicity slag (C/S = 4.18) is appreciably less than that by low basicity slag (C/S = 1.9), corroded thickness of the former is 1.7 ~ 2.5 mm, but of the latter is 2.5 ~ 4.5 mm.

8.3 HMOR

Under reducing conditions, the effects of boron bearing additives on hot strength (at 1400°C) of doloma-carbon and magdoloma-carbon specimens are insignificant because there is no change in boride in the mass after heating to 1400°C. The HMOR value of specimen DC is very close to that of DO.

Specimens with mixed additives (boron bearing additives and Al additive) exhibit

improved hot strength, irrespective of type of boride (CaB_6 Bc and ZrB_2). With decrease of CaB_6 / Al ratio, hot strength tends to increase. The optimum CaB_6 / Al ratio appears to be 1: 3.

In terms of effectiveness in improving hot strength properties, the order of merit of additives is: metal additives > mixed additives > boron bearing materials.

8.4 Comprehensive Evaluation on the High Temperature Properties

From the above, the effects of boron bearing additives on high temperature properties of doloma-carbon and magdoloma-carbon specimens may be summarized as follows:

Boron bearing additives are very beneficial to increase oxidation resistance, but detrimental to slag corrosion resistance; they have improving effect on hot strength properties under reducing conditions.

Mixed additives (boron bearing additives and metal powder) have noticeably positive effects on both oxidation resistance and corrosion resistance. They also promote increase in hot strength.

8.5 Mechanism of Boron Bearing Additives on High Temperature Properties

The dramatic effect of boron bearing additives in improving oxidation resistance of doloma-carbon and magdoloma-carbon specimens may be attributed to the formation of borate melt protective layer. Oxidation product of boron and metallic boride, B_2O_3 reacts

with calcium oxide to form $Ca_3B_2O_6$ and with magnesia to form $Mg_3B_2O_6$, mostly the former. The borate melt would act as a protective layer, retarding carbon oxidation. With increase in temperature from 1200°C to 1600°C, the amount of borate melt increases accompanied by simultaneous lowering of viscosity, the liquid phase protective layer would thus be formed more readily and more rapidly. The consequence is that under influence of borate melts, oxidation resistance increases with increase of temperature.

In the case of mixed additives (boron bearing additives and metal additive), the synergetic effect of two types of additives on oxidation behavior is observed. There is no reaction between their oxide products that is between $Ca_3B_2O_6$ and $Ca_3Al_2O_6$ predominantly. On the one hand, borate melt acts as a barrier against oxidation as described above, on the other hand, $Ca_3Al_2O_6$ partially filling in the interstices between grains would also impede oxidation, though to a less extent.

In general, the mechanism of slag corrosion on carbon bonded basic refractories is considered to be: carbon oxidation followed by chemical corrosion. The formation of borate melt layer described above, not only retards oxidation, but also impedes slag penetration; this results in very thin reaction zone of specimens with boron bearing additives after corrosion tests. However, after decarbonization, when chemical corrosion comes into important play, the borate melt would be corroded quickly as revealed in the dynamic rotary test.

In the case of mixed additives (boride and metal), the amount of borate melt formed is less and high melting $Ca_3Al_2O_6$ is formed from oxidation of the metal. Therefore, it is important to control the boron content and optimized combination of the two types of

additives would be appropriate.

For HMOR tests, results with calcium boride added in doloma-carbon and magdoloma-carbon specimens, under reducing atmosphere are good, under such conditions, CaB_6 remains stable; it does not react with the oxides (CaO and MgO), nor the carbon (graphite), or Al_4C_3. The same is observed with Bc and ZrB_2 additions. Mixed additives of boron bearing additives and Al powder in a proper ratio (2 : 2 or 1 : 3) would result also in marked improvement of hot strength owing to the synergetic effect of two types of additives. The contribution of Al addition to increase of hot strength is much more than that of boron bearing additives.

8.6 Suggestions

Based on the above research results, we recommend the adoption of mixed additives for optimizing hot strength properties of doloma-carbon and magdoloma-carbon materials. For applications where oxidation resistance is primary requisite, one should chose higher ratio (e.g. 3 : 1) of boron bearing additive and Al (or Mg-Al alloy); for applications where both oxidation resistance and corrosion resistance are important, the choice of a ratio 2 : 2 would be more appropriate; for application where hot strength is important, the choice should be towards the lower ratio (1 : 3).

Our research results have indicated that doloma-carbon and magdoloma-carbon materials with boron bearing additives and its combination with Al (or Mg-Al alloy) additive have a good prospects for developing high performance doloma-based refractories with optimized high temperature properties. It is thus recommended to

pursue this study to establish the kinetics of oxidation of doloma-carbon and magdoloma-carbon with boron bearing additives, to complete the observations on the phase and microstructure changes at different temperatures, in different atmospheres and in contact with different slags, and to search for more economical boron bearing materials as antioxidants (e.g. utilization of colemanite).

The concept of liquid phase protective layer for antioxidation (such as borate melt in our work) should be extended to other carbon bonded materials (such as Al_2O_3–C, Al_2O_3 / ZrO_2–C materials), oxide and non-oxide composites, and even some non-oxide materials. A long term project for fundamental research in this field may be interesting and important and may ultimately lead to the development of a new series of high-tech, high-performance refractory ceramics.

CHAPTER 9: IN SUMMARY

(1). Boron bearing additives have marked effects on improvement of oxidation resistance of doloma-carbon and magdoloma-carbon materials, much better than that of metallic additive (Al powder or Mg-Al alloy). The order of merit as antioxidants is CaB_6 > Bc > ZrB_2 > colemanite > alloy. The optimum addition amount of boron bearing additives for oxidation resistance is 3 ~ 4 %. Mixed additives (boron bearing additives and Mg-Al alloy or Al powder) are also very effective as antioxidants due to synergetic effects of the two types of additives.

(2). The remarkable effect of boron bearing additives on oxidation behavior is found to be attributed to the formation of borate melt protective layer, during oxidation, the borate being predominantly $Ca_3B_2O_6$. This protective layer would impede or retard carbon oxidation in the materials. With increase of temperature, oxidation resistance is observed to increase because the borate melt is formed more quickly and more readily at high temperature (1400°C ~ 1600°C).

(3). Boron bearing additives are found by dynamic rotary test to be negative to slag corrosion of doloma-carbon and magdoloma-carbon materials. This may be due to the effect of borate melt which would be beneficial at first stage of slag corrosion (carbon oxidation), but detrimental at second stage of slag corrosion (chemical corrosion).

(4). Boron bearing additives have no bad effect on hot strength tested under

reducing atmosphere, because under such conditions, they are stable. However, mixed addition of a appropriate ratio of boride and metal additive would noticeably improve strength properties at elevated temperatures under reducing conditions. When boride / Al ratio is 1 : 3, HMOR at 1400°C is almost doubled as compared with specimen without additive. This again is due to synergetic effects of the two types of additives. Contribution of Al additive on hot strength only, always under reducing conditions is the greatest.

(5). Based on the above results, for optimization of high temperature properties (oxidation resistance, corrosion resistance and hot strength) of doloma-carbon and magdoloma-carbon materials with emphasis on antioxidation, it may be concluded that mixed additives of boron bearing additives and metal powder with proper ratio according to the service conditions of applications should be adopted. Developmental work should be considered and organized in this direction.

REFERENCES

1) ZHONG, X. C. (1995). "Refractories Developments for Iron and Steelmaking in China", Refractories (in Chinese), 30 [1] 3 ~ 9, 1996. "Some Comments on Future Refractories Development for Iron and Steelmaking in China" , Refractories (in Chinese), 29 [1], 2 ~ 5.

2) UCHIMURA, R. , KUMAGAI, M., OHISHI, I. (1984). "Development of High Performance Magnesia-C Bricks for BOF", Proc. 27th Inter. Colloquium on Refractories, Aachen, 360~404 .

3) LEVESQUE,J., MAIRESSE, P., WHITLEY, R. D. S. (1984). "Converter Lining: A Compromise between Performance and Economy", Proc. 27th Inter. Colloquium on Refractories, Aachen, 109~114.

4) NARUSE, Y., FUJIMOTO, S., SHIKANO, H., HARADA, T. (1984). " Carbon Containing Bricks for Ladle Slag Line", Taikabutsu Overseas, 4 [2], 49~57.

5) HORIIO, T., FUKUOKA, H., ASANO, K. (1986). " Evaluation of Applicability of Magnesia-C Brick to Converters and its Effect", Taikabutsu Overseas, 6 [1], 11~15.

6) LIPINSKI, T. R., FICHTNERR ., BENECKE, T. (1992). "Study of the Oxidation Protection of MgO–C Refractories by Means of Boron Carbide", Steel Research, 63 [11], 493~495.

7) LIPINSKI, T. R., FICHTNER, R., (1992). "Wetting Conditions and Microstructural Characteristics of a Fired B4C- Containing MgO Carbon Brick", Steel Research, 63 [12], 526~530.

8) RIGAUD, M., LI, X., BOMBARD, P., GUEROULT, B. (1992). " Oxidation Resistance of Carbon-Bonded Basic Refractory Compositions" , Proc. of the 75th Steelmakiing Conference of the Iron and Steel Soc. of the AIME, Toronto, Canada, 307~315.

9) RIGAUD, M., BOMBARD, P., LI, X. (1993). " Phase Evolution in Various Carbon-Bonded Basic Refractories", UNITECR'93, Sao Paulo, Brazil.

10) DAVID A. H. (1994). " Minerals Review — Dolomite", Am. Ceram. Soc. Bull., 73 [6], 95~96.

11) LIN, B., WU, Q. (1989). " Refractory Minerals and Raw Materials", Published by Metallurgical Industry Press, 117~140.

12) ALPER, A. M. (1970). " High Temperature Oxides", Published by Am. Academic Press, Vol. 1.

13) LEVIN, E. M., ROBINS, C. R., MCMURDIE, H. F. (1964). " Phase Diagrams for Ceramists", American Ceramic Society, Columbus, Ohio, 102.

14) GRIFFIN, D. J., RICHMOND, C. (1996). " The Application of Doloma Refractories in Steelmaking Applications", Canadian 35th Annual Conference of Metallurgists, Montreal, Canada.

15) MCGANNON, H. E. (1979). "The Making Shaping and Treating of Steel" , U.S.S., USA, 297~302.

16) COOPER, C. F. (1994). "Refractory Applications of Carbon" , Br. Ceram. Trans. J., 84 [2] 48~53, 1985. 17) W. M. Kenan, E. Allera, "Graphite" ,Ceram. Bulletin , 73 [6], 101~104.

18) LI Nan, ZHANG Wenjie. (1990). " Carbon Composite Refractories" , Published by Science Press, China, 68~103.

19) QIAN Chenxin. (1990). " Graphite and Refractories" , Luoyang Institute of Refractories Research, 1~12.

20) COOPER, C. F. (1980). " Graphite Containing Refractories" , Refractories J. 55 [6] 11~21

21) KELLY, B. T. (1981). "Physics of Graphite", Applied Science Publishers Inc., Englewood, USA, 197~200.

22) BROWN, A., STEIN, G. R. (1983). " The Properties of Ceramic Graphite Bodies" , Refractories J. 58 [2] 7~10.

23) BRANT, P. O. R. C., CRUZ, V. C. (1993). " Brazilian Flake Graphite for Carbon Containing Refractories" , UNITECR' 93, Sao Paulo, Brazil, 401~410.

24) COOPER, C. F., ALEXANDER, I. C., HAMPSON, C. J. (1985). " The Role of Graphite in the Thermal Shock Resistance of Refractories" , Br. Ceram. Trans. J., 84 [2], 57~62.

25) DOUGHTY, G. R., TOVEY, L. S., (1993). " A Comparison of the Oxidation Behavior in Air at 1050 °C of Natural Flake Graphite" , UNITECR' 93, Sao Paulo, Brazil, 830~839.

26) GARDZIELLA, A. "Phenolic Resins, General Economic Account and Application Possibilities, Especially as Binders with High Carbon Yield" , 4th Inter. Carbon Symposium Baden-Baden, 7. (1986).

27) WIESCHE, V., GARDZIELLA, A., SOLOZABAL, SIREN, R. J. (1991). "Synthetic Resins as Carbon Forming Agents for Various Refractories (Carbon Yields, Analytical Methods, Structures and Emissions)", UNITECR'91, Aachen, 260~264.

28) KAISER, A. (1993). "Progress in Preparation of Carbon Containing Refractories Bodies with Different Binding Systems", UNITECR' 93, Sao Paulo, Brazil, 202~210.

29) WILLIAMS, P., TAYLOR, D., LEONI, H. (1993). "Advanced Phenolic Resin Binder Systems for Magnesia-Carbon Refractories" , UNITECR' 93, Sao Paulo, Brazil, 347~359.

30) MCENANEY, B., RAND, B. (1985). "Carbon Binders from Polymeric Resins and Pitch (Structure and Properties of the Carbons) ", Br. Ceram. Trans. J.,84 [6], 193~198.

31) RIGAUD, M. (1994). "New Additives in Carbon-Bonded Refractories", Proc. of the 8th CIMTEC World Ceram. Congress, Florence, Italy.

32) HUNOLD, K. (1995). "Boron Compounds in Carbon-Bonded Refractories" Ceramic Industry, [2], 47~50.

33) LIPINSKI, T. R., WOIF, P. (1993). "Reaction Processes in the Interior of an MgO-Carbon Brick with Boron Carbide Additive", Steel Research, 64 [2], 123~127.

34) RIGAUD, M., RICHMOND, C. (1991). "Oxidation Kinetics of Graphite in Basic refractory Compositions", UNITECR' 91, 383~387.

35) WATANABE, K., YABUTA, K., YAMAMOTO, H. (1995). "Oxidation Behavior of MgO-C Bricks with Various Additives", UNITECR' 95, 100~107.

36) LIPINSKI, T.R., SCHMEIZER, B., UILTZKA, S. (1994). "Tests on the Oxidation Inhibiting Effect of CaB_6 in Refractory MgO-C Materials", Steel Research, 65 [6], 234~237.

37) HANAGIRI, S., HARADA, T., FUJIHARA, S. (1993). "Effects of the Addition of Metal and CaB_6 to MgO-C Bricks for Converters", Taikabutsu Overseas, 13 [3], 20~27.

38) KUWABARA, K., TAKETSUGU, H. (1995). "Refractories Containing ZrB_2", Taikabutsu Overseas, 15 [4], 51~53.

39) YAMAGUCHI, A., TANAKA, H. (1995). "Behavior and Effects of ZrB_2 Added to Carbon–Containing Refractories", Taikabutsu Overseas, 15 [2], 3~9.

40) YAMAGUCHI, A., TANAKA, H. (1991). "Role and Behavior of Non-Oxide Compounds Added to Carbon-Containing Refractories", UNITECR' 91, 19 ~22.

41) "New Boron Additives for Magnesia Carbon Refractories", World Ceram. & Refractories, [3~4] 11~12, 1995.

42) BRANT, P. O. R. C., Lima, W. A., GROENNER, C. A. (1993). "Development of High Erosion and Corrosion Resistance MgO-C Bricks for BOF Applications", UNITECR' 93, 462~471.

43) Li, Xiangmin. RIGAUD, M. (1996). "Oxidation and Corrosion Resistance of MgO-C Refractories with Antioxidants", Proceeding Inter. Sym. on Refractories. Haikou, China, 514~521.

44) SURUGA, T. (1995). "Effect of Mg-B Material Addition to MgO-C Bricks", Taikabutsu Overseas, 15 [2], 25~31.

45) ICHIKAWA, K., TSUKAMOTO, N., NOMURA, O. (1995). "Effects of Mg-B Material Addition to Al_2O_3-C SV Plate", Taikabutsu Overseas, 15 [2], 33~37.

46) SUNAYAMA, H., KAWAHARA, M., MITSUO, T. (1996). "Effects of AlB_2 Addition on the Resistance of Oxidation of MgO-C Refractories", The Pac. Rim 2nd Refractories Conference, Cairns, Australia.

47) YAMAGUCHI, A., ZHANG, S., YU, J., HASHIMOTO, S. (1995). "Behavior of Antioxidants Added to Carbon-Containing Refractories", UNITECR`95, 341~348.

48) OSCROFT, R. J., ROEBUCK, P. H. A., THOMPSON, D. P. (1995). "Characterisation and Range of Composition for $Al_8B_4C_7$ ", British Ceram. Trans. 94 [1], 25~26.

49) ZHAO, Hailei. LI, Wenzhao. ZHONG, Xiangchong. (1995)." Study on Oxidation Resistance of Zirconica-Corundum Mullite / Boron Nitride Composite", Bull. of the Chinese Ceram. Soc., [1] 41~46.

50) CHEN, Zhaoyou (1988). " The Thermodynamical Behavior of Additives in Carbon Containing Refractories", Refractories (in Chinese), 22 [2], 51~56.

51) NARUSE, Y., HIRAGUSHI, K., KIWAKI, S., TAKITA, I. (1986). "Progress on Carbon-Bearing Refractories for the BOF", Ceram. Eng. Soc., 7 [1--2], 109~144.

52) SCHRUFF, F., BERBACH, M. O., MUSCHNER, U. (1992). " High Quality Refractory Materials and Systems for the Clean Steel Technology", Proc. of the 2nd Inter. Symposium on Refractories, Beijing, China, 34 ~53.

53) AMAVIS, R. (1990). " Refractories for the Steel Industry", Commission of the European Communities, Elserier Applied Science Press, 175 ~186.

54) DEGAWA, T., UCHIDA, S., OTOTANI, T. (1987). "Development of CaO-MgO Refractories and Their Effects on Refining Mechanism of Extremely Clean Steel", Proc. 2nd Inter. Con. on Refractories, Tokyo, 842 ~856.

55) HAYASHI, S., TAKANAGA, S., TAKAHASHI, H., WATANABE, A. (1991). "Behavior of Boric Compounds Added in MgO(C Bricks", Taikabutsu Overseas, 10 [3], 12~19.

56) GRIFFIN, D. J., LOEFFELHOLZ, M. D., MILLER, T. G. (1991). "Considerations for the Measurement and Improvement of Oxidation Resistance in Doloma-Carbon and Magnesia-Carbon Refractories", 361~367, UNITECR' 91, (2nd edition).

57) ROTH, R. S., NEGAS, T., et al., (1981). "Phase diagrams for Ceramists", Edited by The American Ceramic Society, 4 Fig. 234, 5154.

58) TAYLOR, H. F. W. (1964). "The Chemistry of Cements", Academic Press Inc., London, Vol. 11, 49~55,

59) LEA, F. M. (1956). "The Chemistry of Cement and Concerte", Edward Arnold (Publishers) LTD., London.

60) BILKERMAN, J. J. (1958). "Surface Chemistry", Academic Press Inc., New York, 23.

61) ZHONG, X. C., LI, G. P., CHEN, Z. Y. (1983). "The Application of Carbon Bearing Magnesitic-Dolomite Refractories for BOF Linings", Proc. of the 1st Inter Con. on Refractories, Tokyo, Japan, 161~169.

62) ZHONG, X. C. (1980). "Some Aspects in the Technical Developments of LD Refractories in China", Acta Metallurgica Sinica, [2] 233~239.

63) HAYASHI, S., OSHIO, Y., WATANABE, A. (1990). "Effect of Metal Additives on Strength of Al_2O_3-C and MgO-C Bricks", Taikabutsu, 42 [11] 681~682.

64) TAFFIN, C., POIRIER, J. (1994). " The Behavior of Metal Additives in MgO-C and Al_2O_3-C Refractories", Interceram, 43 [5] 354~358; [6] 458~460.

65) ZHONG, X. C., SUN, G. C., LIU, X. Y. (1989). " High Temperature Properties of Carbon-Bonded Corundum-Mullite-Zirconia Materials", 1803~1813, UNITECR'89.

66) SHI, G., Sun, G. C., ZHONG, X. C. (1989). "Thermomechanical Properties of MgO-CaO-C Materials", Refractories, (In Chinese), [3] 1~4.

67) LUBABA, N. C., RAND, B., BRETT, N. H. (1989). "Microstructure and Strength of MgO-Carbon Composite Refractory Materials", Br. Ceram. Trans. J., [88] 47~54.

68) SAMSONOV, G. V. (1982). "The Oxide Handbook", IFI / Plenum, 84.

IMAGE EVALUATION
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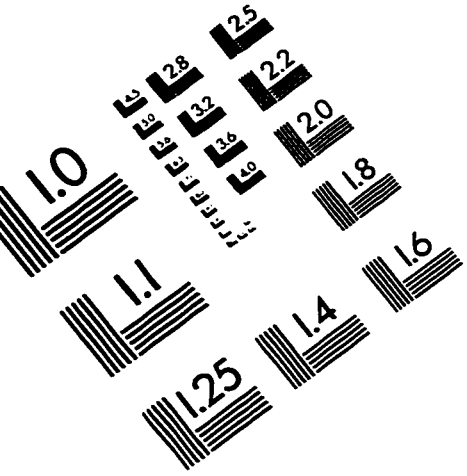

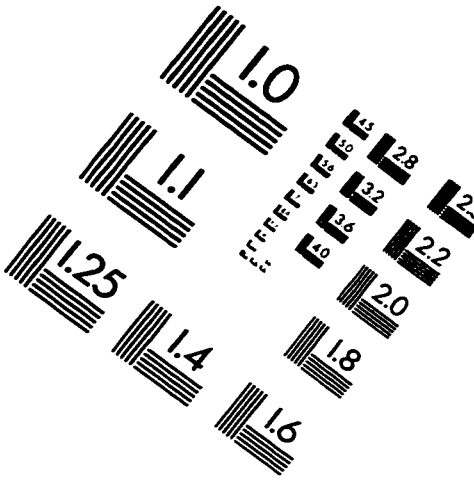

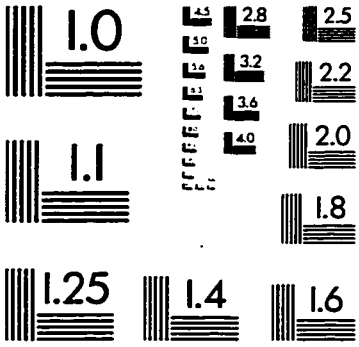

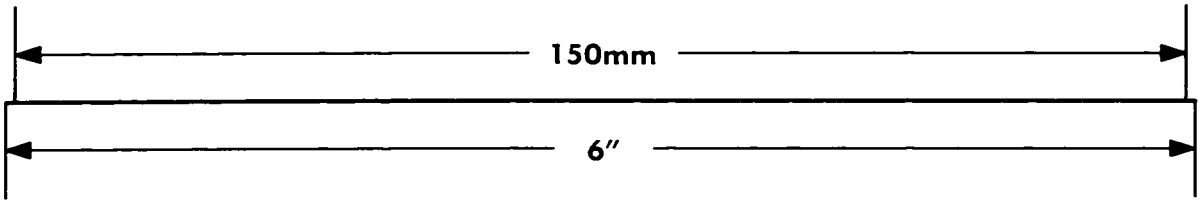

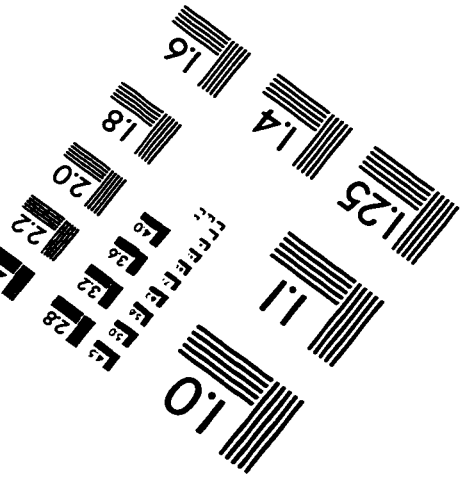

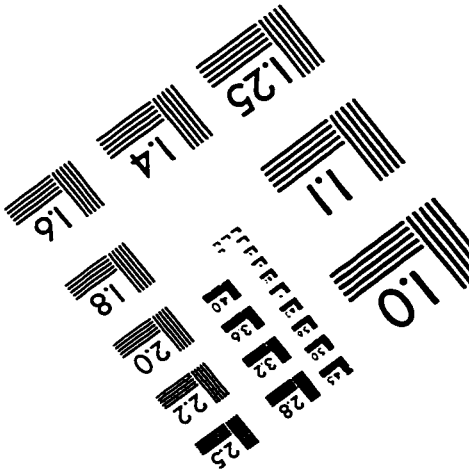

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